INSTITUTE OF
PAPER CHEMISTRY
Appleton · Wisconsin

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS

STUDIES ON HARDWOODS

Project 2500

Report Twelve

A Progress Report

to

THE GRANTORS

May 17, 1971

THE INSTITUTE OF PAPER CHEMISTRY
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SUMMARY

In a brief review of chlorine dioxide-alkali pulp properties described in
previous reports, attention is drawn to changes in pulp behavior on bleaching.
These changes include an increase in initial drainage resistance, a more rapid
increase in drainage resistance on beating, and a marked tendency for handsheet
densities to be confined to a higher density range.

An increase in handsheet density also has been observed when bleaching
multistage chlorine dioxide-alkali pulps. In these pulps no adverse effect was
observed when the chlorine dioxide contained 15% chlorine in place of the chemical
equivalent amount of chlorine dioxide. The occurrence of small shives in screened
pulps and their effect on density is discussed as a characteristic of some pulps,
including those as described in earlier reports. Much greater changes in Canadian
freeness have been observed at different pH levels for chlorine dioxide-alkali pulps
than for a kraft pulp.

The mechanical, chemical, and physical aspects of chip fiberization are
discussed as well as the assessment of fiberized chips for providing chlorine
dioxide-alkali pulps. Previously reported work has been extended to include
fiberization of aspen and red maple chips at different elevated pressures using an
Asplund machine. Microscopic examination of fiberized material provided evidence
that the degree of chip plasticization increased markedly when operating at a steam
pressure equivalent to 158°C. compared with 133°C. Red maple chips heated at the
higher temperature for five minutes were fiberized with almost no change in fiber

length distribution.   Hot-water solubility and other data for aspen and red maple

indicated some chemical changes but no very obvious amount of hydrolysis occurred

under the conditions of chip fiberization.

For sodium chlorite-alkali pulps, chip fiberization conditions can have a

significant influence on Canadian freeness vs. handsheet drainage time relationships.

Other properties influenced include minimum handsheet density, handsheet density

range, rate of increase in drainage time on beating, occurrence of small shives, and

specific scattering coefficient, especially in the case of red maple.   Some

indication of degradation of strength properties was obtained when chips were heated

at 165°C. for 3 minutes before fiberization.

Chlorine dioxide-alkali pulps have been prepared from chips fiberized

under various conditions.   Unbleached red maple pulp yields were 68-72% with 0.8 to

8.0% screen rejects, and bleached pulp yields were 64-67% with over 80 TAPPI bright-

ness.   The lignin modification reaction time varied appreciably with fiberization

conditions.   The properties of chlorine dioxide-alkali pulps from different

fiberized materials do not correlate with those of the corresponding chlorite-alkali

pulps.   Aspen and red maple chlorine dioxide-alkali pulp properties cover a consid-

erable range.   This includes pulps that could be bleached with no decrease in the

time taken to beat and without handsheet densities becoming confined to the higher

density ranges.   Thus, it is demonstrated that lignin removal does not necessarily

lead to bleached fibers that behave like holocellulose fibers.

Process-derived differences related to fiberization conditions, rather

than species-dependent differences, are the source of the range of properties found

for aspen and red maple chlorine dioxide-alkali pulps.   For handsheet drainage time,

breaking length, tensile energy absorption, burst factor, tear factor, and M.I.T.

fold, the range of properties observed in various aspen and red maple pulps reflects

the pattern of the relative positions of the beating time vs. handsheet density curves. Handsheet smoothness at equal handsheet density was found to vary with fiberization conditions which also influenced specific scattering coefficient, especially in the case of red maple. For this, it is believed marked differences observed in light scattering relate in part to variation in the extent of separation into individual fibers. Extreme differences in behavior of the red maple and aspen pulps follow changes in fiberization. The use of different machines for preparing materials does not appear to have introduced some mechanical factor responsible for differences in pulp behavior. Improved properties of red maple and aspen chlorine dioxide-alkali pulps are temperature dependent and, at least in the case of red maple, time dependent with respect to the chip fiberization step. The explanation for the observed improvements in pulp properties is thought to concern some physical factor possibly associated with chip plasticization. It is suggested fibers could have an inherently greater degree of internal strength when chip fiberization is carried out under conditions leading to more desirable pulp properties.

The best aspen and red maple chlorine dioxide-alkali pulps, produced at about 30% greater amount than the corresponding kraft pulps, have fewer screen rejects, greater specific scattering coefficients, longer beating times, and a greater handsheet density range than achieved for aspen chlorine dioxide-alkali pulps described in previous reports. Except for tear factor, smoothness, and specific scattering coefficient, the handsheet properties at a given sheet density approximate those for the corresponding kraft pulps. The excepted properties are at least comparable to those applicable to another commercial pulp. It appears feasible to produce desirable papermaking chlorine dioxide-alkali pulps from hardwoods.

INTRODUCTION

In reviewing previous progress reports attention may be focused on three

aspects, namely:

        1. The raw material,

        2. The method or process of producing pulp, and

        3. The properties of pulps.

Limitations to the position reached with respect to any of these aspects bear on

the successful outcome of this project.

The raw material has been limited to the use of aspen in most of the

investigations reported, although some initial studies on loblolly pine were

described in Report Ten (1).

The method or process of producing pulp based on chip fiberization has

been limited to one set of conditions in previous reports. These conditions were

adopted partly as an expedient taking into account equipment in hand. In addition,

all chlorine dioxide-alkali pulps for which handsheet properties have been obtained

were prepared using essentially chlorine-free chlorine dioxide.

The properties of pulps described in previous reports point to there being

a marked shift in the behavior of bleached compared with unbleached pulps so that

any fully bleached pulp could be of limited acceptability. This shift in behavior,

that is apparently associated with degree of delignification, may be illustrated by

reference to two earlier observations. These are that fully bleached pulps not

only beat several times as rapidly as corresponding unbleached pulps but also

provide handsheets with densities tending to be confined to the higher density range.

To clarify these points, comments on some previous results are included in the

following discussion.

CHLORINE DIOXIDE-ALKALI PULPS AND CHANGES WITH VARYING LIGNIN CONTENT

The chlorine dioxide-alkali Pulps A-D, prepared using the conditions shown in Table I, have been selected to provide a basis for initial comment. A note on the codes used in this report is given in Appendix I.

Unbleached Pulps A and B were prepared with the distinction of using significantly different alkali extraction times, and from the way Pulp C was prepared it may be regarded as a bleached form of Pulp B. Pulp D has a yield and brightness similar to Pulp C. These two comparable bleached pulps were made without and with alkali conditioning, respectively.

Figures 1 and 2 show beating time _versus_ Canadian freeness and handsheet density, respectively, for Pulps A-D. From these figures it is apparent that bleaching to 80 TAPPI brightness can cause a significant decrease in the time to beat to either a low freeness or high handsheet density. Also, it will be seen that bleaching can cause handsheet densities to be confined more to the higher density range. In these respects, the bleached pulps tend to be like holocellulose pulps and for comparison there are included curves for a pulp prepared by sodium chlorite-alkali delignification of aspen pin chips, as described on page 34.

One question concerning the Canadian freeness data for Pulps A-D in Fig. 1 is whether the relationship of the curves to each other is a reflection of drainage properties. On this point, reference can be made to Fig. 3 which is based on an earlier study (Report Eight) (2) of the relationship between Canadian freeness and average drainage resistance of Pulps D-G. This relationship was found to be essentially similar for these pulps over 550-200 C.F. Since Pulps A-D were prepared from identically fiberized chips that were delignified by a similar process, it may be assumed the Canadian freeness _versus_ drainage resistance relationship is essentially similar for Pulps A-D. Therefore, the shift in the freeness curve that is

TABLE I

CONDITIONS USED TO PREPARE CHLORINE DIOXIDE-ALKALI PULPS

Pulp Code[a]	ClO$_2$, %	NaOH, %	Avail. Cl$_2$, %	Time, min.	Final pH	Yield, %	Rejects, % o.d.p.	Klason + Acid-sol. Lignin, %	Brightness, TAPPI
Alkali conditioning – consistency 6.0%; temp. 50°C.									
A-B	–	3.0	–	60	10.5	95.5	–	–	–
C	–	3.0	–	60	10.5	94.6	–	–	–
D-G					nil				
Lignin modification – consistency 6.0%; temp. 25→35°C.									
A-B	9.0	3.5	–	270	3.0	90.7	–	–	–
C	9.0	3.5	–	270	3.0	89.2	–	–	–
D-G	9.0	3.5	–	295	2.6	94.9	–	–	–
Alkali extraction – consistency 8.0%; temp. 60°C.									
Pulp-A	–	6.0	–	10[b]	11.8	73.0	7.0	7.0 estd.	–
Pulp-B	–	6.0	–	240[b]	11.7	69.0	2.8	5.0 estd.	–
C	–	6.0	–	120	11.4	67.6	–	3.7	–
D	–	9.0	–	120	11.7	67.7	–	5.5	
E	–	9.0	–	10	11.9	72.3	–	7.5	
F	–	6.0	–	120	9.3	77.1	–	10.2	–
G	–	6.0	–	10	10.9	81.5	–	11.3	–
Hypochlorite reaction – consistency 12%; temp. 40°C.									
Pulp-C	–	0.25	4.5	>270	7.9	63.1	0.3	1.4	78.0
Pulp-D	–	0.25	4.5	235	7.9	66.2	4.4	3.0	77.5
Pulp-E	–	0.25	4.5	180	7.9	68.2	9.0	4.5	74.0
Pulp-F	–	0.25	4.5	170	8.2	71.6	16.9	6.8	70.5
Pulp-G	–	0.25	4.5	150	8.2	76.8	17.6	8.1	69.0

[a] Pulps A,B = LL-10, LL-240, Rep. 6; Pulps C,D,E,F,G = PP-4, 00-4, 00-2, 00-3, 00-1, Rep. 8.

[b] Reaction temp. 50°C.

Figure 1. Aspen Chlorine Dioxide-Alkali Pulps with Beating Time
vs. Canadian Freeness
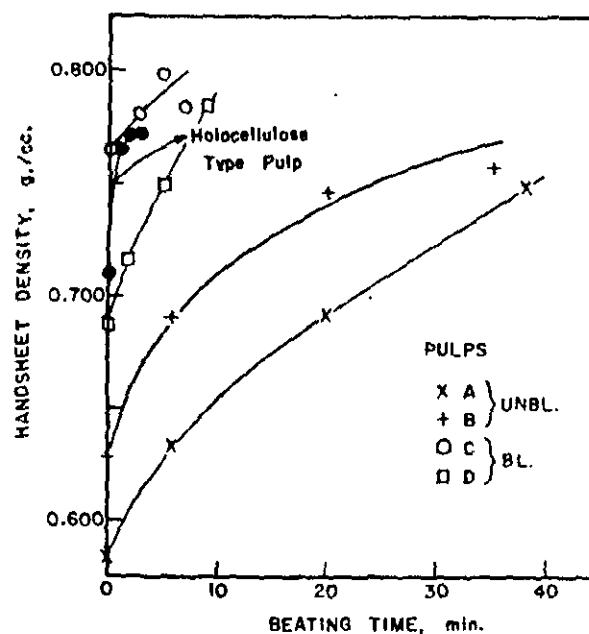
Figure 2. Aspen Chlorine Dioxide-Alkali Pulps with Beating Time
vs. Handsheet Density
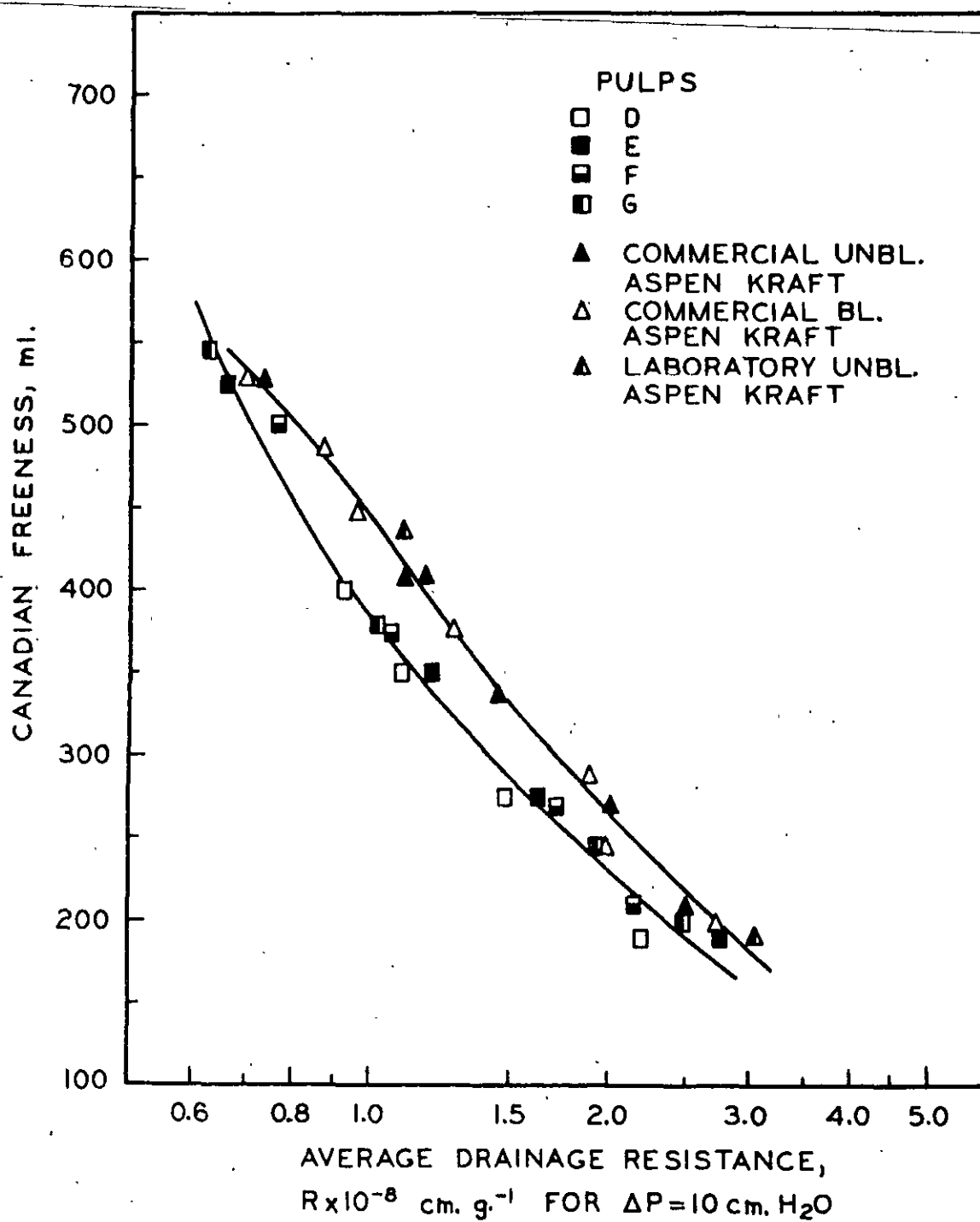
Figure 3. Aspen Chlorine Dioxide-Alkali and Aspen Kraft Pulps with Average Drainage Resistance vs. Canadian Freeness

found when beating a bleached instead of unbleached pulp is indicative of a greater initial drainage resistance and a more rapid increase in drainage resistance on beating.

An important consideration is whether or not the two trends in Fig. 1 and 2 are an inherent part of the process being used to remove lignin.

Consider a situation where, for some reason, as bleaching of chlorine dioxide-alkali pulps progresses the behavior of the pulp fibers always changes and closely approaches the corresponding holocellulose fibers. Then, bleaching to progressively higher brightnesses could mean the pulps would have progressively less versatility.

Alternatively, it could be stated that if a series of pulps were to be produced similarly to Pulp D except that the lignin content and yield were progressively greater, then the pulps would have a slower increase in drainage resistance on beating and handsheet densities would be extended to the lower density range. Pulps D-G in Table I provide an example that fits this situation which is illustrated more fully in Fig. 4 and 5.

The slower increase in drainage resistance on beating pulps with increasing lignin content is paralleled by appreciably longer beating times being needed to swell the pulps. This is shown in Table II.
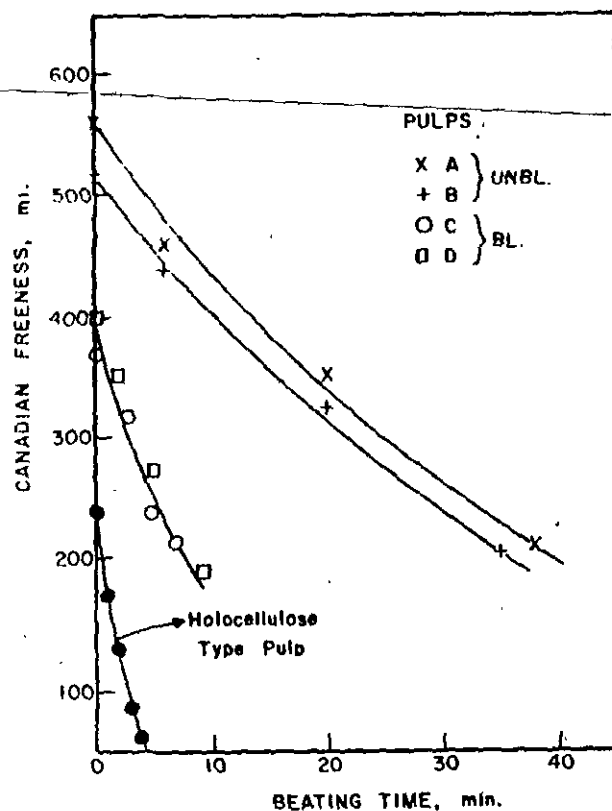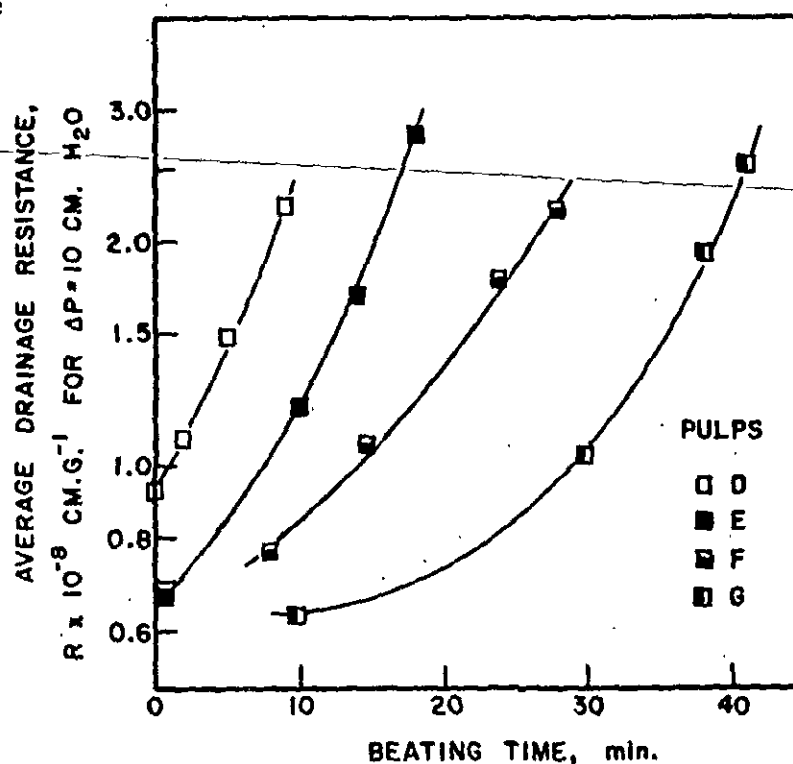
Figure 4.   Aspen Chlorine Dioxide-Alkali Pulps with Beating Time
vs. Average Drainage Resistance
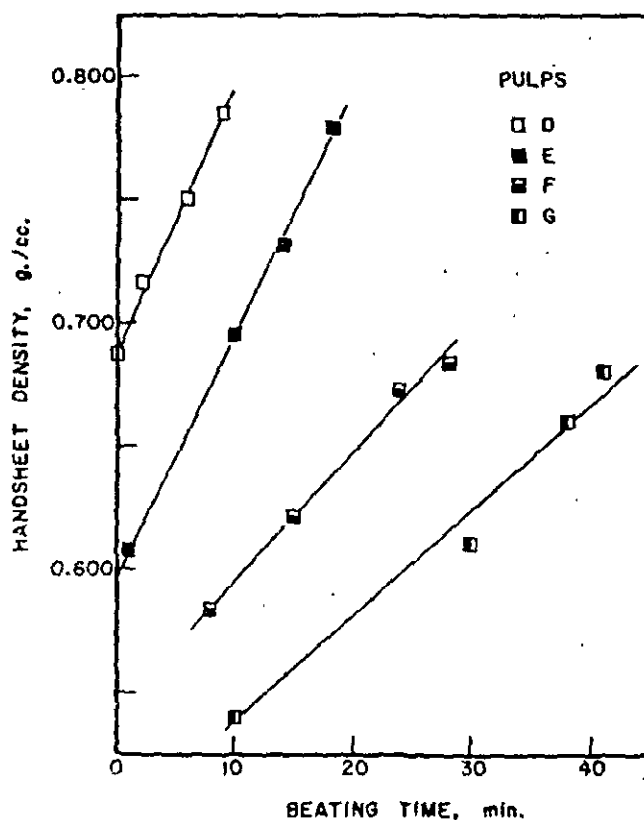
Figure 5.   Aspen Chlorine Dioxide-Alkali Pulps with Beating Time
vs. Handsheet Density

TABLE II

INCREASED PULP-LIGNIN CONTENT WITH INCREASED BEATING TIME
TO SWELL PULPS[a]

Pulp	Lignin Content, %	Beating Time, min.	Specific Volume, $\langle \bar{v} \rangle$, cc./g.
D	3.0	2	2.99
		9	3.34
E	4.5	10	3.12
		18	3.40
F	6.8	15	2.94
		28	3.22

[a] Data from Report Eight.

If the ease with which a pulp swells when beaten reflects the degree of restraint to swelling that is exercised by the presence of cross-linked polymers, then increasing polymer or lignin content might be expected to result in less readily hydrated pulps as illustrated in Table II.   In addition, if increasing lignin content is analogous to greater cross-linking, the swelling capacity of the unbeaten material might be expected to decrease as more lignin is left unremoved. This has been found to apply to Sitka spruce holocellulose made from transverse sections of wood.   When more lignin was left with the holocellulose, the nonsolvent water content for water-logged materials (3) increased as in Table III.

TABLE III

INCREASED NONSOLVENT WATER WITH INCREASED LIGNIN CONTENT

Lignin content, %	1.1	3.3	5.3	10.7
Fiber saturation point, %[a]	180	140	130	94

[a] The fiber saturation point of most species is 30-40%, because of the constant density of wood substance.

From the above, it appears for the process being used to prepare bleached chlorine dioxide-alkali pulps there is a tendency for aspen pulp fibers to become like those of holocellulose. Obviously, it would be an advance to know how this tendency can be prevented. Some evidence has already been described indicating that the handsheet properties of unbeaten softwood holocellulose fibers can be influenced significantly by alkali (4) as, for example, in Fig. 6. Aspen tear factor was not affected in this manner by alkaline pretreatments, possibly because its major hemicellulose components differ from typical conifers. However, a previous comparison of data on chlorine dioxide-alkali pulps prepared with and without alkali conditioning (2) indicated omission of alkali conditioning was associated with relatively lower handsheet densities and thus appears to have some effect on pulp properties.
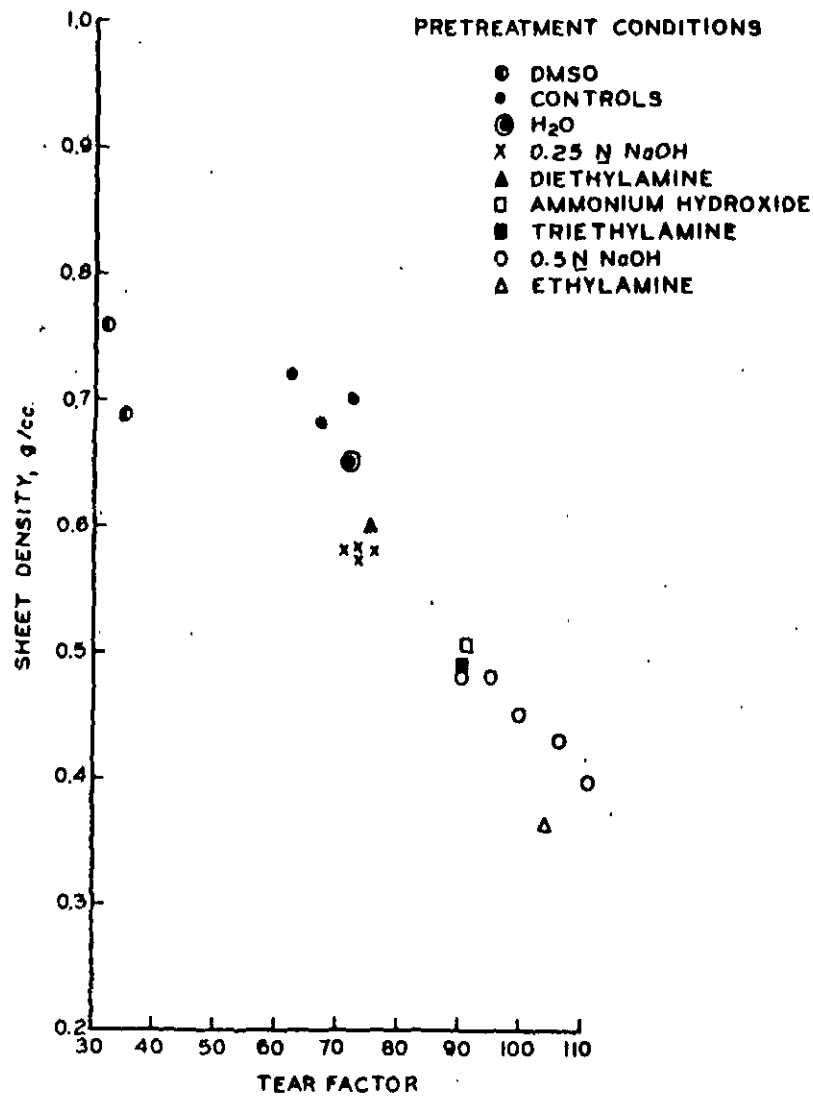
Figure 6. The Relationship Between Sheet Density and Tear Factor for Various Black Spruce Chlorite Holocellulose Handsheets (4)

MULTISTAGE CHLORINE DIOXIDE-ALKALI PULPS WITH CHLORINE
IN CHLORINE DIOXIDE

CHLORINE IN CHLORINE DIOXIDE

Further confirmation of there being a tendency for handsheet densities to be confined more to higher values when a chlorine dioxide-alkali pulp is bleached may be seen in the handsheet density data in Table IV for the unbleached Pulps H or J and bleached Pulps I or K. When, for example, Pulp H was bleached to give Pulp I, the density of handsheets from unbeaten pulp increased from 0.626 to 0.727 g./cc.

Pulps H and J were obtained as described in the experimental part, using conditions associated with two chlorine dioxide reactions as in Table V and with no alkaline conditioning step. The products were screened, then centricleaned before beating the centricleaned accepts and preparing handsheets.

The high percentage of screen rejects recorded in Table V is in accord with the pulp yields being near or above the fiber liberation point. Disintegration (600 rev.) of the rejects obtained from Pulp J reduced the rejects from 18.4 to 8.0% after additional screening. These rejects had Klason lignin 7.1% and acid-soluble lignin 3.2% compared with 3.4 and 2.1, respectively, for the original screen accepts. These and other lignin analyses in Table V reveal the process of delignification was nonuniform in spite of there being two lignin modification and two alkali extraction stages. Such nonuniformity would be a factor in the occurrence of persistent shives which are discussed further in the section entitled Shives.

TABLE IV

ASPEN--HANDSHEET DENSITY DATA FOR CHLORINE DIOXIDE-

ALKALI PULPS H, I, J, AND K[a]

Pulp	Beating Time, min.[b] or sec.[c]	Density, g./cc.
H (unbleached)	0	0.626
	4[b]	0.673
	8[b]	0.720
	16[b]	0.765
I (bleached)	0	0.727
	5[c]	0.768
	25[c]	0.802
	50[c]	0.813
J (unbleached)	0	0.651
	3[b]	0.688
	8[b]	0.725
	12[b]	0.752
K (bleached)	5[c]	0.705
	15[c]	0.735
	25[c]	0.754
	35[c]	0.793

[a] Complete handsheet data are given in Appendix II.

[b] Minutes in Valley beater with 2.0-kg. bedplate load.

[c] Seconds at 25% s.c. with 3.4-kg./cm. beating pressure, PFI mill.

TABLE V

CONDITIONS USED IN PRODUCING PULPS H AND J[a]

Pulp	ClO$_2$[b], %	NaOH, %	Cl$_2$, %	Temp., °C.	Time, min.	Final pH	Yield, %	Klason + Acid-Sol. Lignin, %[c]
Lignin modification — consistency 6.0%								
H	4.97	--	0.88	25→35	115	2.0	98.9	16.1 + 6.7
J	5.38	--	--	25→35	155	2.3	98.9	15.7 + 7.0
Alkali extraction — consistency 10%								
H	--	6.0	--	70	20	9.5	82.3	9.2 + 3.4
J	--	6.0	--	60	20	9.8	82.2	9.4 + 3.6
Lignin modification — consistency 10%								
H	2.53	--	0.45	25→35	150	2.2	80.2	5.9 + 4.5
J	2.72	--	--	25→35	170	2.9	80.5	6.5 + 4.6
Alkali extraction — consistency 15%								
H	--	2.6	--	70	20	9.1	71.5[d]	2.6 + 2.2
J	--	2.6	--	60	20	10.1	72.9[e]	3.4 + 2.1

[a] Starting material: fiberized aspen (see experimental part).

[b] All percentages on an o.d. fiberized chip basis unless shown otherwise.

[c] Mean of two analyses in all cases.

[d] C.F. 380 at pH 7.0; screen rejects 8.4% o.d.p. (Klason lignin 4.4%; acid-sol. lignin 3.2%). Pulp H was disintegrated (200 rev. counts in British disintegrator) before screening.

[e] C.F. 410 at pH 7.9; screen rejects 18.4% o.d.p. (Klason lignin 5.7%; acid-sol. lignin 2.8%). Pulp J was disintegrated (200 rev. counts) after screening.

Bleached Pulps I and K were obtained by reaction with hypochlorite under the conditions given in Table VI. The brightness of Pulp I is significantly higher than for previously evaluated bleached pulps such as Pulps C and D in Table I prepared with a one-step lignin modification. For Pulp I, the brightness approximates that reached using essentially comparable conditions in earlier small-scale experiments (Report Nine, Table VI) (5) with a two-step lignin modification.

Pulp I was made from the flat-screened, centricleaned material as used to prepare handsheets identified with Pulp H, and thus, Pulps H and I have identical fiber populations which should be noted in regard to Table IV. On the other hand, Pulp K was flat screened and centricleaned after bleaching, in the same way as unbleached Pulp J so that Pulps J and K could have differing fiber populations.

While bearing in mind any possible differences in fiber populations, the handsheet data in Appendix II reveal no evidence of degradation associated with the hypochlorite reactions detailed in Table VI. Also, there is no indication of any detrimental effect when the chlorine dioxide contains chlorine on an 85:15 (w/w) basis and this mixture is used instead of the chemical equivalent amount of chlorine dioxide. This is of considerable importance because it is simpler and cheaper to produce chlorine dioxide without having to reduce the chlorine content below 15%.

It is noted that the delignification procedure for Pulps H and J (Table V) had no alkali conditioning and the extractions were for relatively short times without much excess alkali. These conditions might be expected to lead to relatively lower handsheet densities in view of previous data related to the influence of alkali conditioning referred to above. However, the results in Table IV for the bleached pulps (Pulps I and K) provide no support for this expectation in that handsheet densities again tend to be high. Thus, the broader explanation of the

TABLE VI

HYPOCHLORITE REACTION DATA FOR PULPS I AND K

Pulp identification	I[a]	K[b]
Hypochlorite, avail. Cl_2, %	——3.0——	
Sodium hydroxide, %	0.8	0.4
Temperature, $^{\circ}C$.	——40——	
Consistency, %	20	18
Time, min.	70	110
Final pH	8.2	8.8
Yield, % o.d. input	95	94
Klason lignin, %	0.75	1.9
Acid-soluble lignin, %	0.25	1.7
TAPPI brightness (water)	83	80[c]
TAPPI brightness (aged)	77	77
TAPPI brightness (ethanol)	88.5	84[c]
TAPPI brightness (aged)	84	81
Canadian freeness, ml. (pH)	290	240 (7.2)

[a] Treatment before hypochlorite reaction identical with that for Pulp H and included flat screening followed by centricleaning.

[b] Hypochlorite reaction on 72.9%-yield product as in Table V with flat screening (7.2% screen rejects; Klason lignin 5.8%, acid-soluble lignin 2.8%) and centricleaning after reaction.

[c] After flat screening and disintegration with acid wash.

trends in Fig. 1 and 2 being related in some way to the process used to remove

lignin should be considered.

SHIVES

The occurrence of persistent small shives or small bundles of unseparated

fibers that pass through a flat screen can result in a rough sheet surface on the

blotter side.   Such shives may interfere not only with the determination of hand-

sheet density but also with the sheet's performance properties.

If shives are present, the handsheet density values calculated using

apparent caliper measurements tend to be low.   This means that much of the handsheet

has a higher density than recorded and in reality the sheet is bonded to a greater

extent than it would have been at the recorded density.   Since strength properties

are markedly influenced by sheet density, the presence of shives, therefore, can

lead to a situation where comparison of handsheet data for a chlorine dioxide-alkali

pulp containing shives with data for a kraft pulp without shives may be misleading.

If handsheet densities for sheets from the different pulps are calculated

by using caliper measurements and also by using mercury displacement measurements,

in principle it is possible to demonstrate more positively whether a between-pulp

comparison of handsheet data at comparable caliper-based sheet density could be

misleading.   Assuming there is no interference from shives, the curve of caliper-

based density vs. mercury displacement density should be the same for both pulps.

If shives lead to an apparently low caliper-based sheet density, then this curve

will be correspondingly displaced.

An indication of the possible extent of interference with handsheet density

determination is provided in Fig. 7 and Table VII.
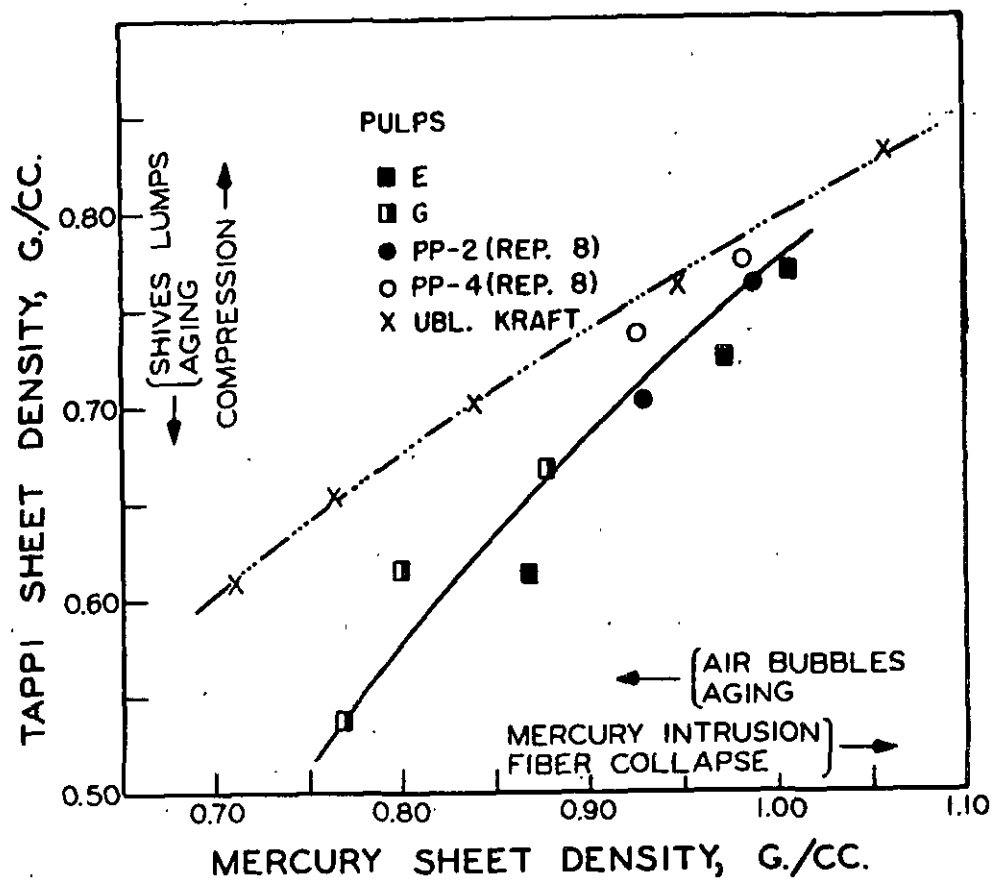
Figure 7. Aspen Chlorine Dioxide-Alkali Pulps and Aspen Kraft
Pulp Data for Mercury Sheet Density vs. TAPPI Sheet Density

TABLE VII

TAPPI HANDSHEET DENSITIES OF KRAFT AND ClO$_2$-NaOH PULPS
AT GIVEN MERCURY HANDSHEET DENSITIES

Mercury, g./cc.	TAPPI Handsheet Densities, g./cc.		% Apparent Underestimate ClO$_2$-NaOH, g./cc.
	Kraft	ClO$_2$-NaOH	
0.76	0.65	0.53	23
0.82	0.69	0.60	15
0.92	0.75	0.70	7
1.01	0.80	0.78	3

To provide some measure of surface roughness, the Bendtsen smoothness values given in Table VIII have been obtained on handsheets prepared after beating Pulps H, J, and K in a Valley beater and Pulps J and K in a PFI mill. The higher the smoothness value, the rougher is a sheet. Hence, it can be seen that unbleached and bleached pulps had relatively rough blotter-side or back-side surfaces even after appreciable beating in either a Valley beater or PFI mill.

The following handsheet tabs (Fig. 8) illustrate the roughness of their wire sides. A loss in opacity is also discernible. This corresponds to a significant reduction in the scattering coefficient from 255 to 171 (see Appendix II).

Thus, for example, Pulp H, which had been screened and centricleaned before beating, is characterized by the occurrence of small shives. When the pulp was beaten enough to reduce the shive content, there was a significant loss in sheet opacity. This phenomenon is not eliminated by reaction with hypochlorite and is regarded as a potential shortcoming for good papermaking of the chlorine dioxide-alkali pulps described so far in this and previous reports.

TABLE VIII

BENDTSEN SMOOTHNESS DATA FOR HANDSHEETS FROM PULPS H, J, AND K

Stock consist., %	Valley Beater			PFI Mill		
	1.57			25		
	Beating Time, min.	Bendtsen Smoothness, ml./min.		Beating Time, sec.	Bendtsen Smoothness, ml./min.	
		Top Side	Back Side		Top Side	Back Side
Pulp H	0	187	1850	-	-	-
	4	99	1140	-	-	-
	8	45	890	-	-	-
	16	20	810	-	-	-
	22	18	950	-	-	-
Pulp J	0	230	2020	10	95	1930
	3	137	1310	30	59	1880
	8	52	990	60	47	1560
	12	27	930	-	-	-
Pulp K	0	254	1990	5	92	1680
	3	195	1520	15	81	1680
	4	44	1050	25	49	1810
	8	31	1050	-	-	-

Valley Beater

4 min.   22 min.

Figure 8.   Handsheet Tabs from Pulp H

CANADIAN FREENESS VERSUS pH AND PULP HISTORY

Somewhat unexpectedly, the unbeaten Canadian freeness values for Pulps H

and J before screening were 380 and 410 compared with 560 and 515 for Pulps A and B

after screening.

Subsequently, centricleaner accepts from Pulp J were extracted with hot

alkali (final pH 11.1) and freeness of the distilled-water-washed pulp determined

at different pH values by appropriate addition of alkali or acid.   Results were

obtained as illustrated in Fig. 9 and additional comment is made in Appendix III.

Because changes in pH can result in much greater freeness changes for the

case of chlorine dioxide-alkali pulps than for a kraft pulp, the observations

depicted in Fig. 9 are noteworthy from a practical viewpoint.   A similar phenomenon

has been referred to by others (6) in connection with delignified cold soda pulp.
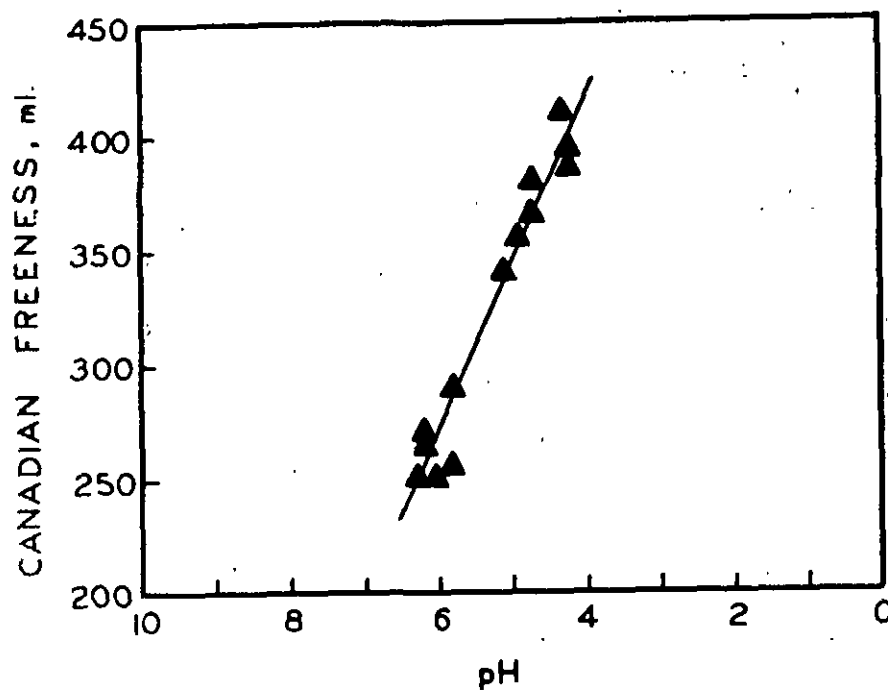
Figure 9.   Canadian Freeness vs. pH Relationship for Aspen
Chlorine Dioxide-Alkali Pulp

FIBERIZATION CONDITIONS, PRODUCT EXAMINATION AND OBSERVATIONS
ON CHLORITE-ALKALI PULPS

To remove the limitations of previous investigations being based on one

set of chip fiberization conditions and on one hardwood, namely aspen, consideration

has been given to the effect of using alternative conditions to fiberize aspen and

red maple. This has also served the purpose of providing information needed in

connection with a possible pilot operation.

CONSIDERATION OF FIBERIZATION

The objective of chip fiberization in this work may be stated as being:

to separate wood into fiber bundles or undamaged fibers

through breaks in the region of the compound middle

lamella in the process of providing a desirable,

selectively delignified papermaking pulp.

There is no expectation that the fiber bundles or undamaged fibers would

be suitable for papermaking without some further processing to provide bonding

properties.

Obviously, other possible materials such as a mechanical pulp would be

expected to have too many broken fibers and a Masonite-type pulp would be expected

to be excessively degraded. Thus, in considering the use of alternative fiberizing

conditions, mechanical, chemical, and physical factors need to be taken into account

concerning how to fiberize in accord with the objective.

Machine design and operation are the two main mechanical aspects. The

design needed is one that gives a machine the capability of being fed with moist

chips somewhere above 100°C. so they will be in a plasticized state when fiberized,

as discussed further below.

Chemical aspects of chip fiberization relate mainly to changes of conse-
quence that may occur in either the carbohydrates or lignin.   Obviously, by heating
with steam under pressure for a long enough time, extensive hydrolysis of carbohy-
drates not only could lead to a degraded pulp but may produce water-soluble moieties
and loss of yield.   Likewise, it is conceivable that lignin could participate in
thermal condensation reactions, for instance.   Because these would involve the more
reactive sites, it is possible there could be noticeable associated changes in the
response of fiberized chips to delignification and/or bleaching.   Just exactly what
changes would occur is somewhat conjectural.   However, significant chemical changes
in either the carbohydrates or the lignin should be discernible from a study of
appropriate data.   For example, the hot water solubility of fiberized chips should
provide some indication of the extent of carbohydrate degradation.   Also, changes
in the ability to delignify and/or bleach should provide a guide to the occurrence
of significant lignin changes.

Physical factors involved in chip fiberization may be considered in terms
of morphological changes, the physical state of the material, and the nature of the
applied forces.   The gross morphological changes or mode of chip breakdown may be
represented as in Fig. 10.   Physical state during chip breakdown and its general
relationship to other factors including temperature, moisture content, and morpho-
logical changes to fibers may be represented as in Fig. 11.

There have been a number of studies relevant to refiner pulping that
include consideration of factors covered in Fig. 10 and 11.   These have been re-
viewed recently (7) and a more extensive discussion may be found in that review.

In aiming for the objective of chip fiberization in this work, it is
advantageous to be able to assess the material produced so as to relate its
character to the factors involved in its production.   This would facilitate an

CHIPS

↓

MATCHSTICKS

| ALIGNED CYLINDERS | FIBER BUNDLES ↓ UNREFINED PULP | STRESSED IN TORSION |
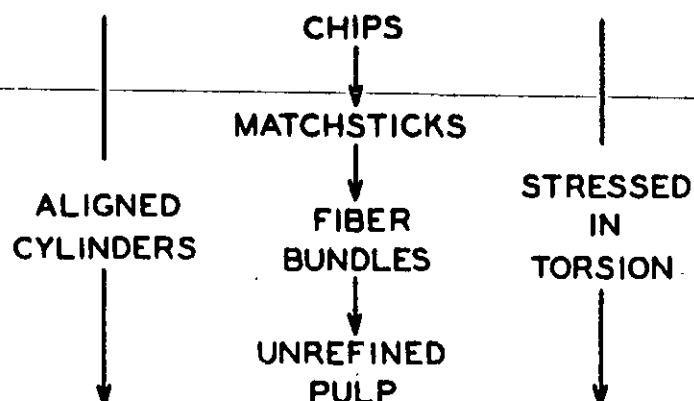
Figure 10. Representation of Progressive Chip Breakdown Occurring with
a Positive Alignment of Material Stressed in Torsion

PLASTICIZED STATE
(VISCOELASTIC)

↑

HIGHER | TEMPERATURE

HIGHER MOISTURE CONTENT

MORE BETWEEN | FIBER BREAKS

FEWER ACROSS | FIBER BREAKS

VARIED WITHIN | FIBER CHANGES

LESS POWER

UNPLASTICIZED STATE
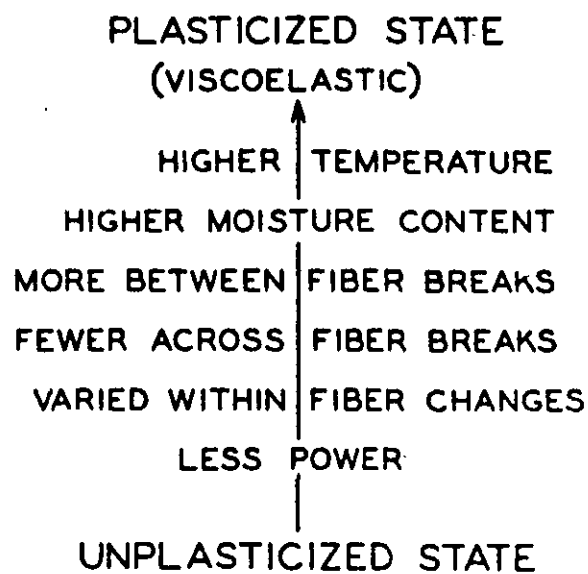
Figure 11. Representation of Changes in Named Factors with
Respect to Physical State During Chip Breakdown

intelligent choice in making any changes to chip fiberization conditions where these influence pulp quality.

In assessing fiberized chips, the following may be considered:

uniformity,

degree of chop (across-fiber breaks),

end tufting of fiber bundles or individual fibers,

extent of fibrillation and vessel damage (between-fiber breaks),

compression and unwinding of fibers (within-fiber change),

fiber length distribution, and

pulp changes.

Uniformity is a desirable quality in fiberized chips to minimize chlorine dioxide consumption while achieving uniform lignin modification and acceptable screen rejects. When these contain chips, as illustrated in Fig. 12, they may reflect inadequate machine design in that the plates may have been forced apart during chip fiberization. This mechanical factor is regarded as primarily responsible for the presence of the chips shown. To obtain some quantitative guide on uniformity, Bauer-McNett classification data as shown in Table IX may be determined. Such data may be interpreted on the provisional basis that on-6-mesh material tends to be coarse enough to contribute to pulping screen rejects, and through-65-mesh material includes some broken fiber fragments.

TABLE IX

BAUER-McNETT CLASSIFICATION OF FIBERIZED ASPEN CHIPS
AS USED TO PREPARE PULPS A AND B

Screen	On-6-Mesh	On-12-Mesh	On-35-Mesh	On-65-Mesh	Through 65 (by diff.)
%	11.8	22.4	35.8	9.4	20.6
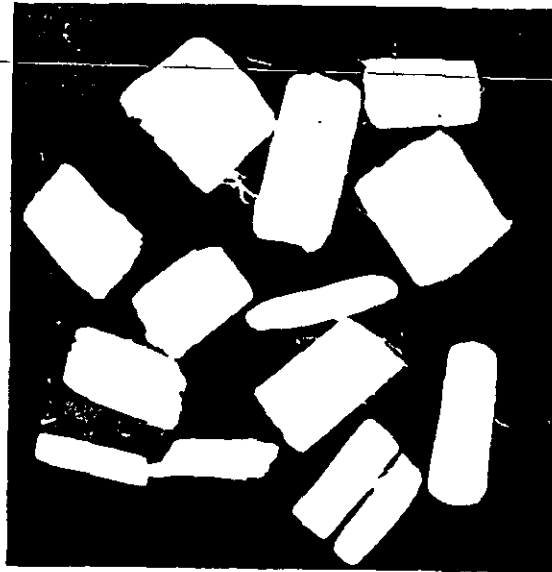
A
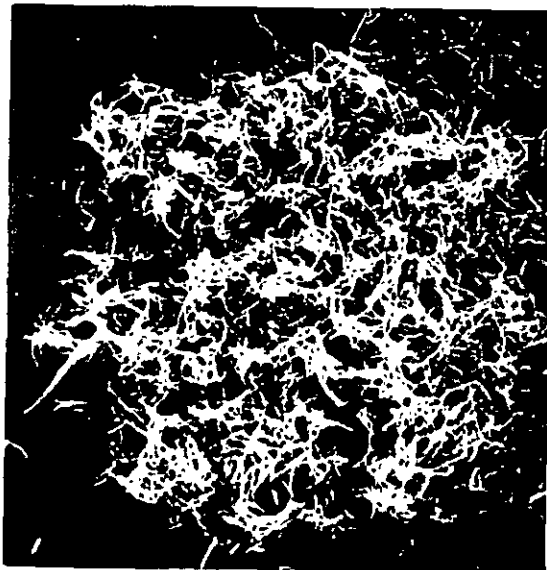
B
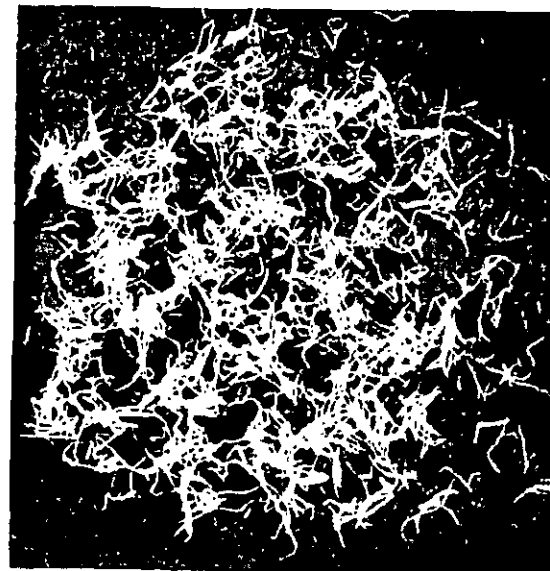
C

Figure 12.   Screen Rejects from Pulp J.   All Magnifications x 1.   A: Most of
the Chips in the Total Screen Rejects (18.4% o.d.p.) from About 2.0 kg. o.d.
Fiberized Chips.   B: Sample of Chip-Free Part of Total Rejects.
C: Sample of Rejects (8.0% o.d.p.) After Disintegration
of Material as in B

Mechanical factors like plate pattern and plate gap influence classification data, as will the physical factors of temperature and moisture content.

The degree of chop provides a ready indication of across-fiber breaks which it is expected should be minimized. Some appreciation of the occurrence of chop can be gained by looking at the material on a blue glass or under a microscope. Physical state is an important factor influencing across-fiber breaks (Fig. 11).

End-tufting of fiber bundles is also affected by physical state, and brushed-out fibers at the end of a fiber bundle would tend to indicate an unplasticized state during chip breakdown. As between-fiber breaks are facilitated by plasticization of the compound middle lamella, end-tufting diminishes.

The extent of fibrillation, as observed by microscopic examination of fractions of delignified pulps is a more rigorous indicator of between-fiber breaks. Apparently, a greater degree of fibrillation is accompanied by more damage to vessel elements when they are present.

Compression and, particularly, unwinding of fibers are two within-fiber changes that may be observed during microscopic examination. Such within-fiber changes have been related to morphological factors and the influence of torsional stress. However, as a general rule, a high proportion of unraveled fibers would not be expected to occur in fiberized chips since the objective calls for a choice of operating conditions that fall short of appreciable work being done on fibers.

Fiber length distribution of chlorite-delignified, fiberized chips, as discussed in Report Ten, is a precise way to determine the extent to which across-fiber breaks have occurred. This provides quantitative evidence in contrast to any qualitative observation on chop.

Pulp changes of consequence that can be associated with chip fiberization might be important. Changes due to mechanical factors appear conceivable. For instance, uniformity could affect screen rejects; excessive fines would probably increase handsheet density and cause some handsheet strength properties to decrease; and a reduction in fiber length could cause a drop in tear factor. Changes due to physical state also appear conceivable in terms of Fig. 11, but the effect of the time chips are heated at temperature and the temperature during chip fiberization on other pulp properties is unclear at this point.

Machine Used

At this stage it appeared the best machine to use for chip fiberization was a 20-in. Asplund Defibrator as illustrated in Fig. 13.

This machine is equipped with a steam preheating vessel that can be operated at over 100 p.s.i. At the bottom of the preheater there is a regular screw feeder to transport heated chips under pressure to a single-disk refiner from which the product is discharged to a cyclone. If, as an expedient, the preheater is operated on a batch basis, when the screw feed to the refiner is started after the chips have been heated for a particular time, those chips first through will have a shorter retention time than the last chips through. While this method of operation is not ideal, it permits the use of a wider range of conditions compared with simply feeding at atmospheric pressure, as previously.

Size and ready availability of the machine were two further favorable factors. In addition, it was judged that purchase of such a machine was unjustified at present as an alternative to using a machine in Stockholm.
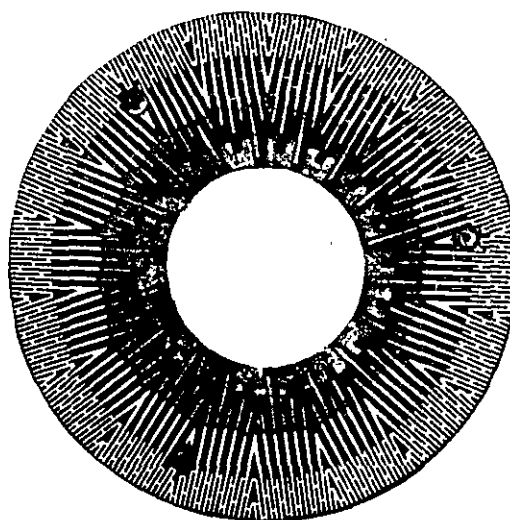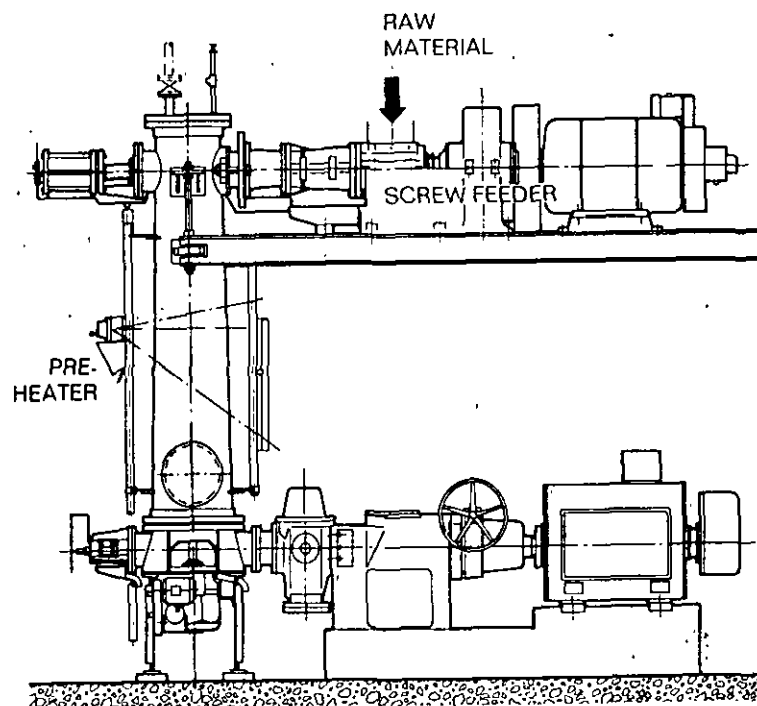
Figure 13. Equipment Similar to that Used in Fiberization Studies, with
Illustration of Plate Pattern Shown Below. Actual Equipment
had no Screw Feeder to Preheater

FIBERIZATION OF ASPEN AND RED MAPLE

Approach

    The approach followed in fiberizing chips in the Asplund machine was that of endeavoring as a first step to make a product like the fiberized aspen used before when producing the pulps referred to in Tables I and V. Thus, water-impregnated aspen chips were steamed under pressure in the preheater and the pressure reduced before feeding the chips to the refiner with other conditions as for L, M, and N in Table X. The product made using a disk gap of 0.016 in. was judged by on-the-spot assessment of uniformity, chop, and end-tufting in fiber bundles to be about comparable to that used previously. Products obtained with a 0.012 and 0.024-in. disk gap looked too fine and too coarse, respectively. Subsequent Bauer-McNett classifications confirmed these assessments and demonstrated that M in Table X had a classification similar to that in Table IX. It is noted the fiberized aspen as classified in Table IX was produced with a disk gap of 0.025 in. on the I.P.C. Bauer machine used at an earlier date. Obviously, a similar setting on the above Asplund machine gives a material with a significantly different classification.

    In the main, aspen and red maple chips were fiberized using a 0.016-in. disk gap. However, the chips were now held at the preheating pressure while being fed to the refiner instead of reducing the pressure as before. As the material from a particular batch of chips was discharged to the atmosphere from the refiner via the cyclone, it was collected for a half or one third of the near-6-min. feed period. The steam pressures at which aspen and red maple chips were heated for different times are included in Tables X and XI.

TABLE X

ASPEN FIBERIZATION

Chip impregnation: Steamed twice at 14 p.s.i. for 2 min., then cold-water impregnated 30 min. at 78-86 p.s.i.

Initial m.c., % wet basis				42			
Final m.c., % wet basis				67-69			

Preheating and fiberization: Asplund OVP Defibrator (batch-fed preheater and screw-fed defibrator)

Preheating pressure, p.s.i.g. or (°C.)		71(158)				86(165)	
Time to pressure, sec.		45				55	
Time at preheating pressure, min.		3.0		1.5		0	
Fiberizing pressure, p.s.i.g. or (°C.)	28(133)			71(158)		86(165)	
Feed period, min.	0-3.0	3.0-6.0		0-1.5	2.8-4.1	0-1.5	2.8-4.1
Time at pressure, min.	as above			1.5-3.0	4.3-5.6	0-1.5	2.8-4.1
Disk gap, 0.001 in.	12	16	24		16		

Bauer-McNett classification, % o.d.f.c.[a]

On 6 mesh	6	14	57	17	15	18	5
On 12 mesh	23	22	13	22	21	20	19
On 35 mesh	34	29	16	27	26	28	31
On 65 mesh	17	16	7	15	16	17	23
Through 65 mesh (by difference)	20	19	7	19	22	17	22

Hot-water solubility, %[b]	--	2.9	3.1	3.3	3.9	--	4.7

Chlorite-alkali delignification[c]

Alkali conditioning[d]	nil	10% NaOH; 60 min. at 50°C.					
Chlorite oxidation	nil	100% NaClO$_2$; init. pH 4.4; 20 hr. (temp. 53°C. after 4 hr.)					
Alkali extraction	nil	5% NaOH; 60 min. at 25°C.					
Yield, %	nil	61	60	59	61	59,59	61.61
TAPPI brightness (ethanol)	nil	n.d.	84	90	n.d.	85,90	89,88

Code	L	M	N	O	P	Q	R

[a] Water temperatures: 21-22°C.

[b] TAPPI Standard Method T 207 m-54.

[c] Pin chips: yield 63%, TAPPI brightness (ethanol) 85.9; chlorite oxidation time 24 hr.

[d] All three steps at 8-10% consistency.

TABLE XI

RED MAPLE FIBERIZATION AND CHLORITE DELIGNIFICATION

Chip impregnation: Steamed twice at 14 p.s.i. for 2 min., then cold-water impregnated 30 min. at 78-86 p.s.i.

	S	T	U	V	W	X
Initial m.c., % wet basis	———— 30-33 ————					
Final m.c., % wet basis	——— 59 ———		——— 60[a] ———		——— 57 ———	

Preheating and fiberization: Asplund type OVP Defibrator (batch-fed preheater and screw-fed defibrator)

	S	T	U	V	W	X
Steam pressure, p.s.i. or °C.	——28 or 133——		——71 or 158——		——86 or 165——	
Time to pressure, sec.	——— 45 ———		——— 45 ———		——— 55 ———	
Time at pressure, min. (i + ii)	1.5-3.0	4.3-5.6	1.5-3.0	4.3-5.6	0.0-1.5	
(i) Time to feed, min.	1.5	4.3	1.5	4.3	0	
(ii) Feed time, min.	1.5	1.3	1.5	1.3	1.5	1.3
Disk gap, 0.001 in.	———— 16 ————					

Bauer-McNett classification, % o.d.f.c.[b]

	S	T	U	V	W	X
On 6 mesh	21	21	9	8	8	5
On 12 mesh	23	23	18	18	19	18
On 35 mesh	24	22	25	24	26	27
On 65 mesh	10	10	20	19	16	18
Through 65 (by difference)	22	24	28	31	31	32
Hot-water solubility, % o.d.f.c.[c]	2.8	2.6	3.1	3.0	3.0	2.9

Chlorite delignification[d]

	S	T	U	V	W	X
Alkali conditioning[e]	———— 10% NaOH; 60 min. at 50°C. ————					
Chlorite oxidation	100% NaClO$_2$; initial pH 4.3; 8 hr. (temp. 38-42°C. after 4 hr.)					
Alkali extraction	———— 5% NaOH; 60 min. at 25°C. ————					
Yield, %	60	58	60	57, 57	60	55
TAPPI brightness (ethanol)	80	87	80	88, 85	81	87
Code	S	T	U	V	W	X

[a] Some chips had 2.5 hr. longer water impregnation.

[b] Water temperatures: 20.5 to 22°C.

[c] According to TAPPI T 207 m-54.

[d] Pin chips: yield 65%; TAPPI brightness (ethanol) 83.9. Chlorite oxidation time 24 hr.

[e] All three steps at 8-10% consistency.

Physical Factors and Visible Fiber Changes

When examining the classification in Table IX, the classifications for O-R in Table X and those for S-X in Table XI, it can be seen that while no classification in Tables X and XI is actually identical with that in Table IX there is a general similarity. At the same time, there is 2 to 20% more through-35-mesh material in the Asplund-fiberized chips. The larger amounts of this finer material tended to be produced at the higher fiberization temperatures, especially for red maple. Here there was a corresponding decrease in on-6-mesh material. The distinct change in classification for material produced at 158 or 165°C. compared with the lower temperatures of 133°C. (Table XI) would indicate plasticization occurs to a significant extent between 133 and 158°C. for red maple. A similar phenomenon would be expected in aspen, but the data in Table X do not cover aspen preheating and fiberization at 133°C.

Microscopic examination of the on- and through-65-mesh Bauer-McNett fractions of S-X in Table XI for red maple revealed more fiber bundles and more evident fibrillation in S and T compared with U-X, as illustrated in Fig. 14. In this, one pair of photographs shows the lesser degree of separation into individual fibers that occurred at 133 compared with 158°C., as, for instance, in the on-65-mesh fractions. The other pair of photographs demonstrates a higher degree of "fibrillation" in the individual fibers at 133 compared with 158°C., as clearly seen in the through-65-mesh fractions. These fractions also include vessel elements which were noticeably more fractured at a fiberization temperature of 133 compared with 158°C. The above observations are in keeping with the degree of plasticization having increased markedly between 133 and 158°C.

A

B

C

D

Figure 14. A and B are from the on-65-Mesh Bauer-McNett Fraction of Fiberized Chips S and U, Respectively, While C and D are from the Through-65-Mesh Fraction of Fiberized Chips T and V, Respectively. Dry Mount, Unstained Samples; Magnification 35x

Differences arising from there being a shorter period of preheating before fiberization were not particularly apparent in red maple.   Nevertheless, there was some indication fewer vessels remained intact in U compared with V.   In the aspen, preheating less before fiberization revealed not only more fiber fibrillation but fewer whole vessels.   This influence of time is illustrated by Fig. 15.

The greater incidence of fiber bundles observed in Bauer-McNett fractions of S and T compared with U-X would be indicative of more across-fiber breaks in the former, which is an expected effect of temperature represented in Fig. 11.   In the same comparison, more evident fibrillation is thought to reflect greater tearing of fibrils during between-fiber breaks for a less plasticized state.   The observation of fewer whole vessels or greater within-vessel changes being associated with more fiber fibrillation in aspen after about 2 compared with 5 min. at 158°C. (Fig. 15) is also regarded as reflecting a change in the degree of plasticization.

Although a similar observation was not clearly discerned for red maple, fiber length distribution data obtained on chlorite-alkali delignified pulps (Table XI) support there being more across-fiber breaks in U compared with V.   For S, U, and V, the first had most across-fiber breaks as seen from Fig. 16.   From the same figure it is concluded also that, since V has very nearly the same fiber length distribution as fiber from pin chips, the amount of through-65-mesh fraction in Table XI should not be interpreted as a measure of broken fiber content.

A   B

Figure 15.   A and B are from the on-65-Mesh Bauer-McNett Fraction of Fiberized
Chips O and P, Respectively.   Dry Mount, Unstained Samples;
Magnification 35X
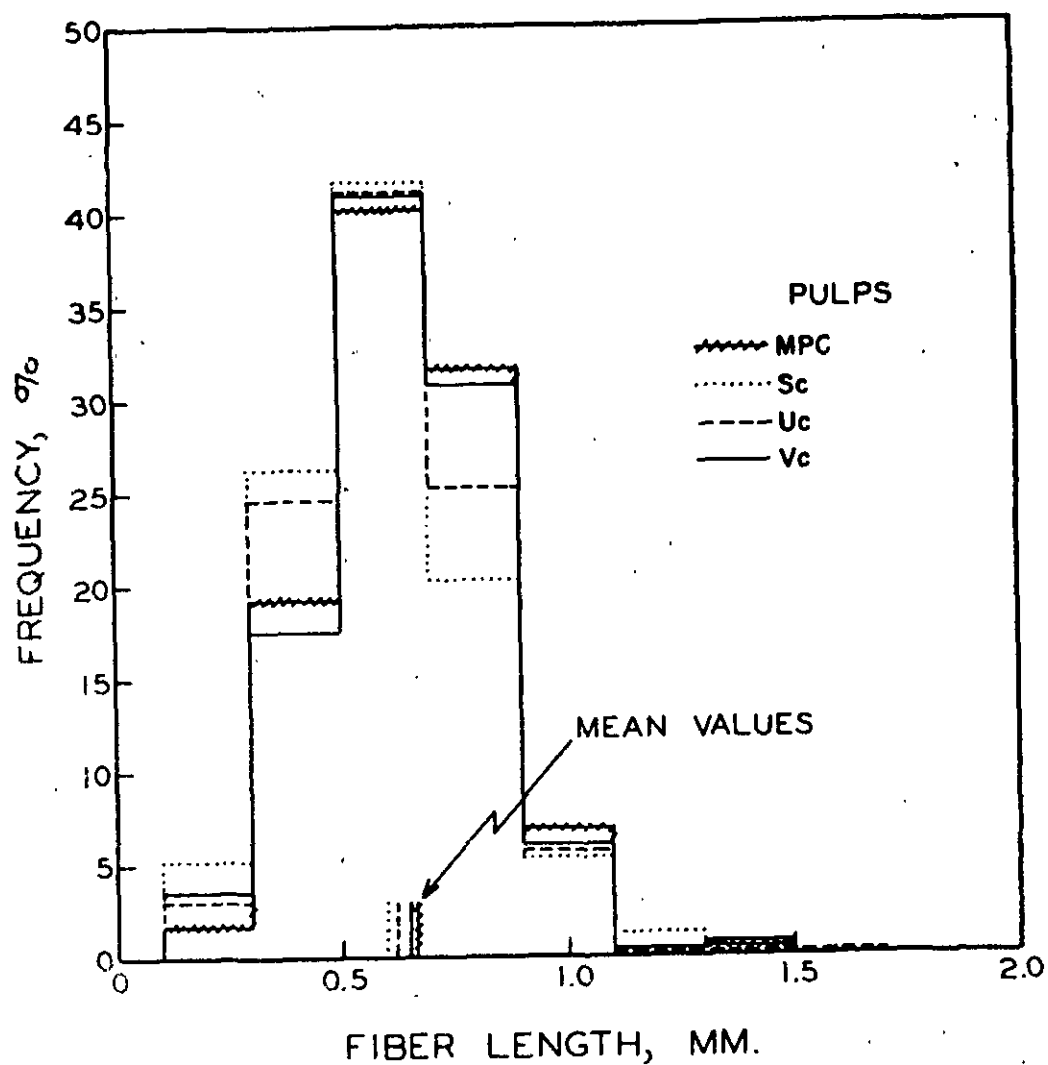
Figure 16. Red Maple — Fiber Length Distribution of Unbeaten
Chlorite-Alkali Pulps Sc, Uc, Vc, and MPC (Pin Chips)

DIFFERENCES OBSERVED IN CHLORITE-ALKALI PULPS

There is some evidence from the hot-water solubility data in Table X that aspen was increasingly converted to hot-water-soluble components with increase in the temperature used during fiberization. No corresponding loss in yield was observable after chlorite-alkali delignification. On the other hand, with red maple (Table XI) there was no apparent corresponding increase in hot-water solubility with increase in the fiberization temperature. Also, the data reveal a relatively lower yield after chlorite-alkali delignification for longer times at the fiberization temperature, and there is an increase in the brightness of the chlorite-alkali delignified pulps corresponding to this relatively lower yield. A similar relationship is not discernible from the data available for aspen. These observations indicate that under the conditions of chip fiberization there are occurring some chemical changes but no very obvious amount of hydrolysis. The exact nature of the chemical changes has not been determined. Nevertheless, the changes associated with up to 8 point differences in brightness, for example, could be significant.

The procedure used for chlorite-alkali delignification was adopted from the work of Thompson and Kaustinen (4). They used chlorite-alkali pulps from conifers to reveal differences in handsheet properties related to various treatments before delignification. In this work, most of the aspen and red maple chlorite pulps in Tables X and XI, respectively, have been beaten in a Valley beater and handsheet properties obtained as in Appendix IV. The data for aspen show a general similarity. After consideration of other results to be presented and discussed below, it has been concluded that this information on aspen fails to reveal potential differences related to chip fiberization conditions. It is believed that this may be associated in some way with species and/or duration of the reaction with sodium chlorite as referred to again later on.

For the case of red maple, the beater evaluation and handsheet properties

disclosed some critical differences.   These are discussed further in the following

paragraphs.

Bearing in mind the possibility of Canadian freeness data for various

pulps being differently related to drainage properties, handsheet drainage times

were determined when evaluating the chlorite-alkali pulps.   Figure 17 for the aspen

pulps provides some evidence of different relationships existing for Canadian free-

ness vs. handsheet drainage time.   However, a considerable amount of scatter in the

data for Pulp Rc weakens the evidence.   For the red maple chlorite-alkali pulps,

Fig. 17 convincingly reveals different relationships of freeness and drainage time.

This observation may appear contradictory to the results as in Fig. 3.

The differences between the two situations seem to lie in species characteristics

and/or fiberization conditions.   In the case of red maple, the curves for Pulps Sc,

Uc, and Wc are virtually coincident and the curves for Pulps Tc, Vc, and Xc are

closely grouped.   The first group is differentiated by having a shorter heating

time at 133, 158, and 165°C.   Thus, chip fiberization conditions have a significant

influence on Canadian freeness vs. handsheet drainage time, at least for red maple.

There is no parallel between this case for red maple and that for aspen, as far as

chlorite-alkali pulps are concerned.

Obviously, unlike the case for chlorine dioxide-alkali pulps covered in

Fig. 3, Canadian freeness provides an unsuitable basis for comparing the aspen set

of handsheet properties as in Appendix IV.   Therefore, no figure comparable to

Fig. 1 has been provided.

Another possible basis for comparing handsheet properties is density.

For each of the chlorite-alkali pulps as in Appendix IV, handsheet density vs.
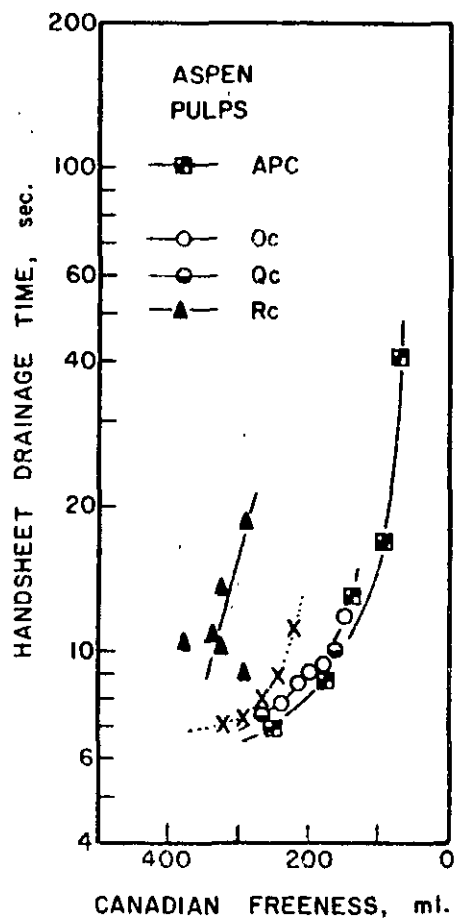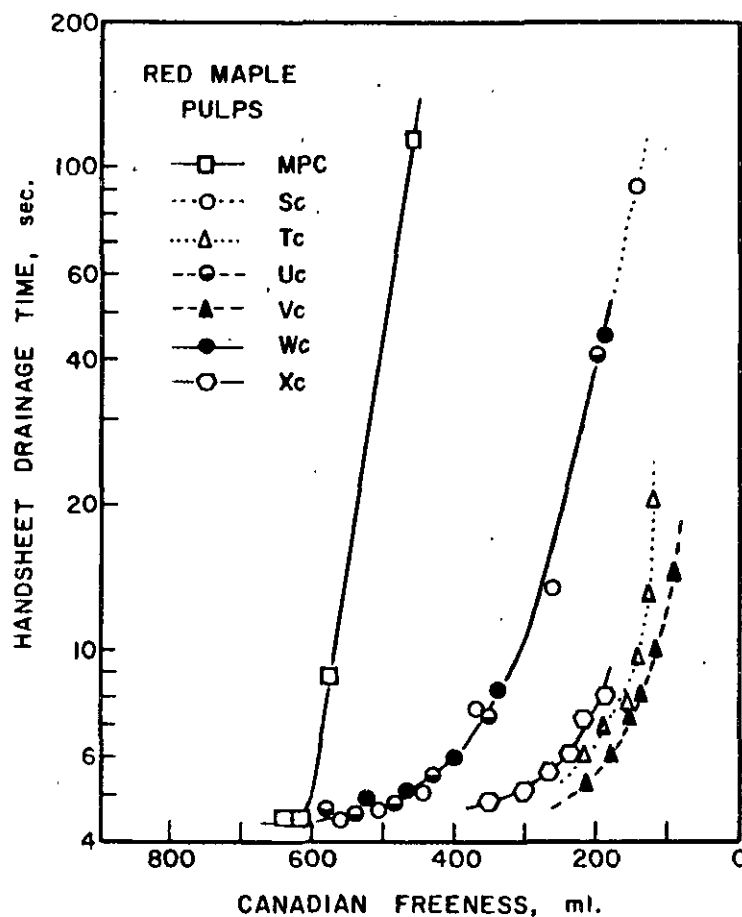
Figure 17. Aspen (a) and Red Maple (b) Chlorite-Alkali Pulps
Showing Canadian Freeness vs. Handsheet Drainage Time

beating time is shown in Fig. 18.   It is clear from these curves that the results

for aspen and maple differ markedly.   The former are grouped together, whereas

there is a considerable spread for red maple.   Because the conditions for fiberizing

O, P, and Q (Table X) correspond with those for U, V, and W (Table XI), the differ-

ences in Fig. 18 must be a reflection of species and/or some other factor, possibly

the duration of the oxidation.

In view of the recognized uncertainty the occurrence of small shives can

introduce to handsheet density data, interpretation of the differences in Fig. 18

needs caution.   To facilitate interpretation, blotter-side smoothnesses in Table

XII may be taken into account.   From these values, where a larger number means a

rougher sheet, it will be apparent that data for Pulps Tc, Vc, and Xc show handsheets

to be about equally smooth, with those for Pulp Wc a little rougher.   On the other

hand, Pulp Sc handsheets are by far the roughest with Pulp Uc next.   Thus, curves

in Fig. 18 for Pulps Tc, Vc, Xc, and probably Wc can be compared without confusion

from persistent shives, whereas it is likely that this does not apply to curves for

Pulps Sc and Uc, especially at lower densities.

As noted in connection with Fig. 2 and 5, when bright, low-lignin-content

chlorine dioxide-alkali pulps were prepared from aspen, handsheet densities tended

to be high and to increase relatively rapidly on beating.   This still applies to

the case of aspen chlorite-alkali pulps, as illustrated in Fig. 18.   For red maple

Pulps Tc, Vc, and Xc (the chips for which were fiberized at 133, 158, and 165°C.

after heating for about 5 min.) each has an increasingly lower minimum handsheet

density of about 0.74, 0.69, and 0.68, respectively.   For Pulp Wc, the chips for

which were fiberized at 165°C. after heating for about 0.75 min., the minimum hand-

sheet density was down to 0.65.   If density ranges are considered for handsheet

drainage times of up to, say, 14 sec., fiberization after a longer time at temperature
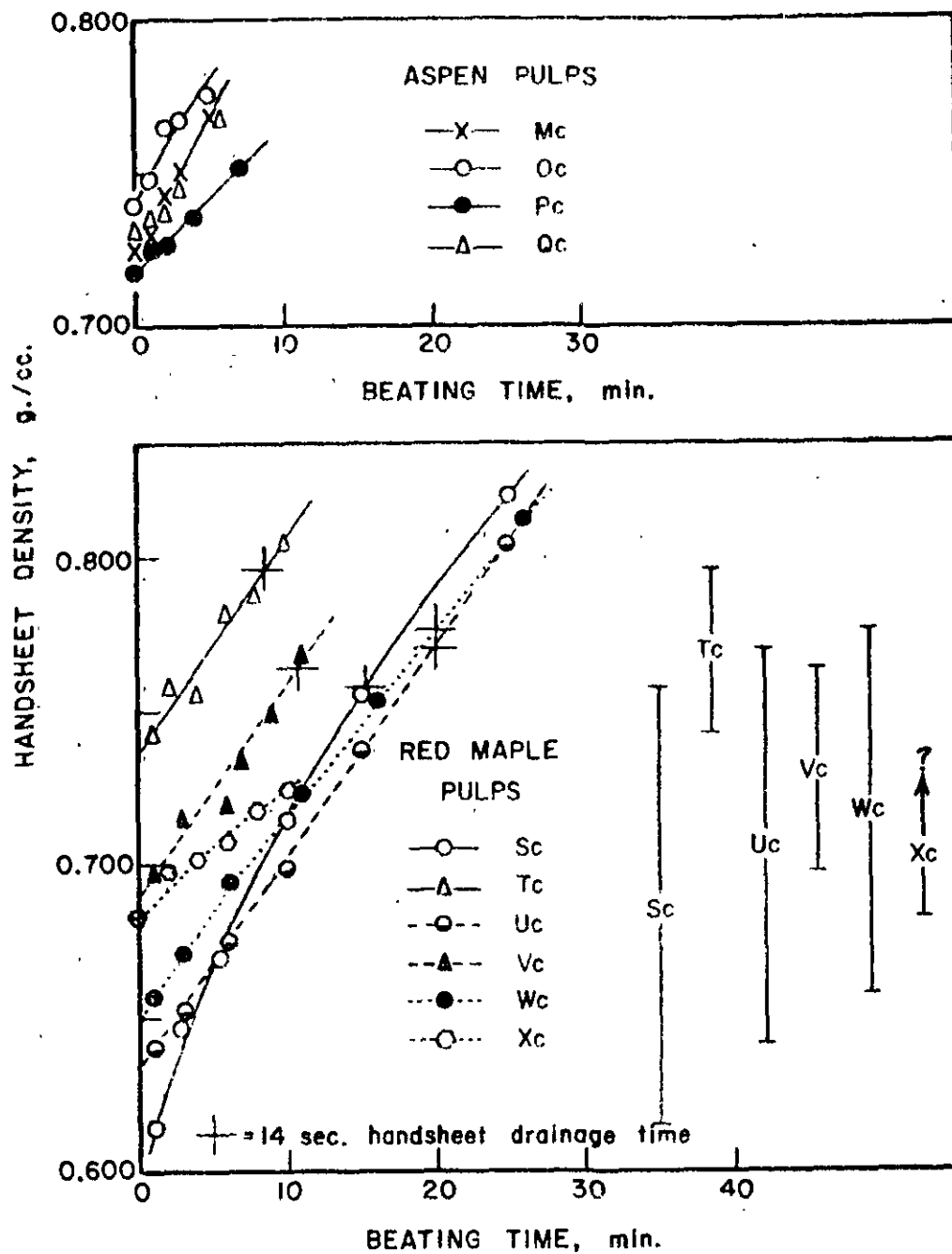
Figure 18. Aspen (Upper) and Red Maple (Lower) Chlorite-Alkali Pulps.
Beating Time vs. Handsheet Density

TABLE XII

RED MAPLE - HANDSHEET DATA FOR CHLORITE-ALKALI PULPS.

Fiberization temp., °C.	133				158				165			
Beating time, min.[a]	1	6	10	15	1	6	10	15	1	6	10	15
Pulp	Sc				Uc				Wc			
Time at fiberizing temp., min.	1.5-3.0				1.5-3.0				0-1.5			
Handsheet drainage time, sec.	4.5	5.2	7.5	13.5	4.6	4.8	5.5	7.2	4.8	5.0	5.7	7.7
TAPPI density, g./cc.	0.614	0.680	0.715	0.755	0.641	0.673	0.699	0.735	0.658	0.693	0.716	0.745
Bendtsen smoothness, back side, ml./min.	2650	1770	1390	1320	1390	940	1070	780	810	770	720	540
Specific scattering coefficient	200	210	190	165	250	250	230	200	270	260	240	220
Breaking length, km.	5.6	7.8	9.1	10.0	6.2	7.5	8.4	9.3	6.8	7.8	8.5	9.4
Tensile energy absorption, g.cm./cm.²	34	80	109	124	48	77	97	124	64	86	96	125
Zero-span breaking length x yield/65, km.	14	16	16	17	16	17	17	18	16	17	17	17
Tear factor x yield/65	57	57	56	55	63	64	63	63	61	62	62	60
M.I.T. fold	40	180	450	950	35	90	200	450	35	95	200	430

Pulp	Tc				Vc				Xc			
Time at fiberization temp., min.	4.3-5.6				4.3-5.0				1.5-3.0			
Handsheet drainage time, sec.	6.2	9.7	21	n.v.[b]	5.3	7.4	13.6	n.v.[b]	5.0	6.1	8.2	n.v.[b]
TAPPI density, g./cc.	0.742	0.776	0.806	n.v.	0.697	0.728	0.758	n.v.	0.688	0.711	0.724	n.v.
Bendtsen smoothness, back side, ml./min.	530	600	620	n.v.	420	470	540	n.v.	450	460	500	n.v.
Specific scattering coefficient	250	220	190	n.v.	280	250	220	n.v.	290	280	260	n.v.
Breaking length, km.	9.1	9.8	10.1	n.v.	8.0	8.7	9.0	n.v.	7.5	8.3	8.8	n.v.
Tensile energy absorption, g.cm./cm.²	112	120	128	n.v.	87	107	117	n.v.	75	90	110	n.v.
Zero-span breaking length x yield/65, km.	17	17	17	n.v.	17	16	16	n.v.	15	15	16	n.v.
Tear factor x yield/65	62	57	56	n.v.	63	64	62	n.v.	53	57	60	n.v.
M.I.T. fold	130	240	410	n.v.	80	160	270	n.v.	50	75	90	n.v.

[a] Valley beater with 2.0-kg. bedplate load.
[b] n.v. = no value.

led to a narrower range as seen by comparing the curves for Pulps Tc, Vc, and Xc with those for Pulps Sc, Uc, and Wc. This applies even if the range of handsheet densities for Pulps Sc and Uc are assumed to be inflated by, say, 20% by the presence of shives.

Figure 19 shows that for red maple Pulps Sc-Tc, Uc-Vc, and Wc-Xc, in each pair a longer time at temperature also led to a more rapid increase in drainage time on beating.

Therefore, at least for red maple chlorite-alkali pulps, fiberization temperature and heating time at that temperature can significantly alter the minimum handsheet density, the handsheet density range, and the rate of increase in drainage time on beating.

The Bendtsen smoothness values of the blotter side of red maple handsheets as recorded in Table XII have been referred to above in considering the relative incidence of shives in chlorite-alkali pulps. Differences inferred by smoothness values are also visible to the naked eye. It is noted that the Bauer-McNett classification data (Table XI) and microscopic examination of fractions as discussed in connection with Fig. 14 both indicated S and T were coarser than U-X which were made at higher temperatures. The smoothness characteristics in Table XII follow a different pattern. In this case there is a significant reduction in the occurrence of fiber bundles or small shives even at the lowest temperature, when heating time was longer.

The handsheets for Pulp Sc illustrated the dilemma that has been posed by previously described aspen chlorine dioxide-alkali pulps. There seems to be a tendency for sheets to have fiber bundles typical of an unbeaten pulp combined with other fibers that typically give a low-opacity sheet. While further beating may
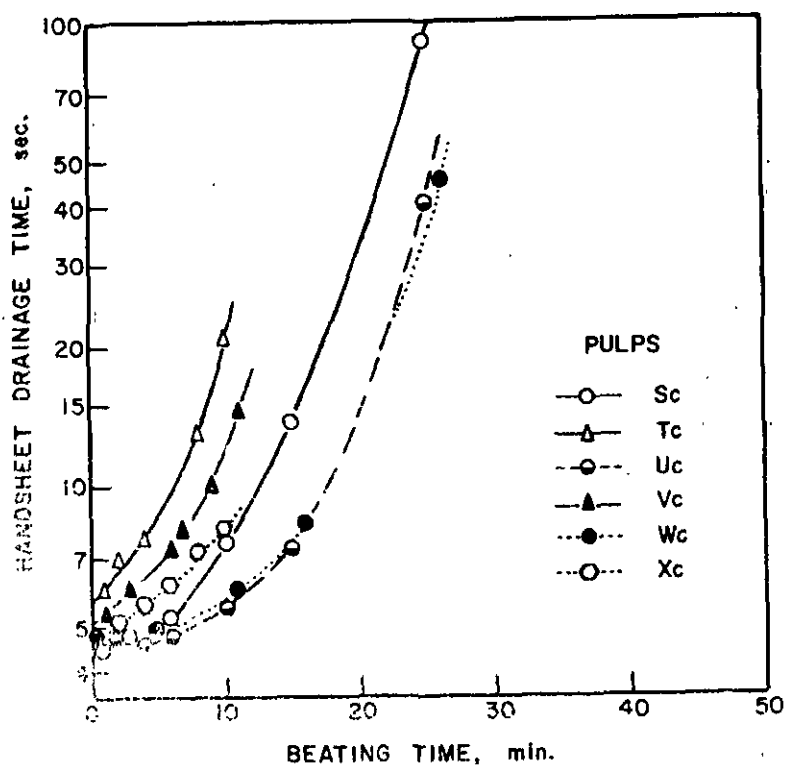
Figure 19. Red Maple Chlorite-Alkali Pulps with Beating Time
vs. Handsheet Drainage Time

tend to reduce the fiber bundle content, unseparated fiber bundles or bundle fragments may persist even when a glassine type of sheet is produced. Recognition of this kind of phenomenon being a problem has been noted by others in chlorine-alkali and chlorine dioxide-alkali delignified cold soda pulps (6).

For the handsheets from aspen chlorite-alkali pulps, the blotter sides were equally smooth, as shown by the data in Appendix IV and the differences discussed below for red maple (Table XII) were not discernible. Since previous aspen chlorine dioxide-alkali pulps are known to have persistent shives, it is thought that their absence in the chlorite-alkali pulps possibly relates to the longer period of oxidation as recorded in Table X compared with Table XI.

Because handsheet strength properties for aspen chlorite-alkali pulps are for relatively high-density handsheets and because the variation in the replicated data for Pulp Rc is unexpectedly high (Appendix IV), between-pulp differences are of questionable significance and discussion is put aside.

On the other hand, for the handsheet strength properties of red maple pulps there appear to be significant between-pulp differences. These may be illustrated through the data as included in Table XII.

Handsheet drainage time, handsheet density, and blotter-side smoothness are influenced by fiberization conditions as discussed already. Clearly, specific scattering coefficient and handsheet strength properties are also affected when considered on the basis of equal beating time. For specific scattering coefficient the extent of the effect is considerable. The highest scattering coefficient data are for handsheets from pulps fiberized at higher temperature for longer times, but in the case of Pulp Xc there is possibly some evidence of degradation. More particularly, zero-span breaking length, tear factor, and M.I.T. fold fail to reach the

maximum level achieved by Pulp Wc, for example.   Comparably low zero-span breaking

length and tear factor data for Pulps Sc and Xc are ascribed to Pulp Sc having been

fiberized without complete plasticization, as already discussed.

It is concluded that, at least for red maple, chip fiberization conditions

are capable of very significantly influencing the properties of the pulps produced

by delignification with chlorite-alkali.   Corresponding effects were not observed

for aspen.

SIGNIFICANCE OF FIBERIZATION CONDITIONS IN CHLORINE DIOXIDE-ALKALI
PULPING OF HARDWOODS

In this part of the project two hardwoods, namely red maple and aspen, have been considered using mainly the fiberized materials discussed in the previous part.

DELIGNIFICATION PROCEDURES

For red maple, the delignification process first used has two lignin modification steps, each of which has a subsequent alkali extraction step. This approach has permitted the preparation of unbleached pulps that have been separately bleached in one stage with hypochlorite. In this way it is possible to separate the influence of bleaching from other process steps.

Preliminary experimental data on chlorine dioxide-alkali pulping of fiberized red maple, as in Appendix V, led to the selection of conditions for the preparation of unbleached and bleached pulps as in Table XIII. The alkali conditioning step was included because with it there was about half the amount of screen rejects after PFI milling the pulp (see Appendix V).

It is noted that for Table XIII unbleached pulp yields were 68-72% with 0.8-8.0% screen rejects and bleached pulp yields were 64-67% with over 80 TAPPI brightness. Other points about these pulps will be covered as the discussion proceeds.

To permit comparison of red maple with aspen pulps (to be discussed later) on the basis that chips of both were fiberized in the same way as applicable to aspen Pulp D (Table I) the material for Pulps Yu and Yb in Table XIII was prepared as indicated in Table XIV using the S185 Bauer machine in Appleton.

TABLE XIII

PREPARATION OF RED MAPLE CHLORINE DIOXIDE-ALKALI PULPS
FROM FIBERIZED MATERIALS V, Y, U, S, AND T

Ref.	ClO_2, %	NaOH, %	Avail. Cl_2, %	Time, min.	Final pH	Yield, %	Rejects, % o.d.p.	Klason + Acid-sol. Lignin, %	Brightness, TAPPI
Alkali conditioning — consistency 6.0%; temp. 70°C.									
V	-	1.0	-	10	9.6	98.8	-	27.1	-
Y	-	1.0	-	10	9.3	98.1	-	26.5	-
U	-	1.0	-	10	9.4	96.4	-	-	-
S	-	1.0	-	10	9.7	96.7	-	-	-
T	-	1.0	-	10	9.5	97.5	-	-	-
Lignin modification — consistency 6.0%; temp. 25-35°C.									
V	4.97	nil	0.88	65	2.1	96.3	-	24.6	-
Y	4.97	nil	0.88	67	-	95.2	-	23.5	-
U	4.97	nil	0.88	60	2.2	-	-	-	-
S	4.97	nil	0.88	70	2.3	94.1	-	23.2	-
T	4.97	nil	0.88	55	2.2	97.5	-	-	-
Alkali extraction — consistency 10%; temp. 70°C.									
V	-	5.5	-	20	9.6	81.8	-	15.6	-
Y	-	5.5	-	20	9.8	82.5	-	15.2	-
U	-	5.5	-	20	9.7	-	-	-	-
S	-	5.5	-	20	9.7	81.2	-	14.5	-
T	-	5.5	-	20	9.6	83.3	-	-	-
Lignin modification — consistency 10%; temp. 25-35°C.									
V	2.53	nil	0.45	80	2.7	79.9	-	13.3	-
Y	2.53	nil	0.45	85	2.8	80.3	-	11.3	-
U	2.53	nil	0.45	85	2.7	-	-	-	-
S	2.53	nil	0.45	80	2.8	79.7	-	12.5	-
T	2.53	nil	0.45	95	2.6	80.6	-	-	-
Alkali extraction — consistency 15%; temp. 70°C.									
Vu	-	2.7	-	20	10.4	69.3	3.8[a]	8.8[b]	54
Yu	-	2.7	-	20	10.5	68.4	6.2	6.4	45
Uu	-	2.7	-	20	10.1	69.3	0.8	5.9	-
Su	-	2.7	-	20	10.3	68.4	3.6	6.1	59
Tu	-	2.7	-	20	10.4	71.6	8.0	6.8	54
Hypochlorite reaction[c] — consistency 15%; temp. 40°C.									
Vb	-	0.8	3.0	55	8.4	65.7[d]	-	2.9	84[e] (81)[f]
Yb	-	0.8	3.0	120	8.9	63.9	-	3.3	86 (80)
Ub	-	0.8	3.0	70	8.4	65.0	-	3.4	84 (81)
Sb	-	0.8	3.0	70	8.9	63.7	-	3.1	87 (82)
Tb	-	0.8	3.0	70	9.1	67.0	-	3.5	85 (80)

[a] Dilute acid soak after alkali extraction, followed by 15 sec. at 25% o.d.p. consistency in PFI mill with 3.4-kg. load before screening. Loss on screening for Vu, Yu, Uu, Su, and Tu was 2.5, 4.3, 4.8, 3.0, and ca. 3%, respectively.

[b] Data for screen rejects: 11.1, 10.4, 10.6, 11.6% and n.d. Klason + acid-sol. lignin, respectively, for Vu, Yu, Uu, Su, and Tu.

[c] Screen accepts were used.

[d] Step yields were: 94.6, 93.4, 93.8, 93.2, and 94.4%, respectively.

[e] Ethanol.

[f] Water.

TABLE XIV

S185 BAUER FIBERIZATION OF RED MAPLE[a]

Chip impregnation: Steam 2 min. at 15 p.s.i. and repeat, then
cold-water soak 30 min. at 100 p.s.i.

	Red Maple
Moisture (after impreg.), approx. % wet basis	60
Preheating conditions:	
Steam pressure, p.s.i. or °C.	80 or 163
Time at pressure, min.	3
Fiberization conditions:	
Steam pressure, atm.	1
Time to feed, min.	ca. 1-2
Feed time, min.	ca. 4
Disk gap, 0.001 in.	25
Bauer-McNett classification:	
On 6 mesh, %	24
On 12 mesh, %	20
On 35 mesh, %	26
On 65 mesh, %	13
Through 65 mesh (by difference), %	17
Code	Y

[a] These conditions are essentially the same as those used to prepare
the material for aspen Pulp D.

To consider the interrelationship of species, process, and papermaking properties, four aspen chlorine dioxide-alkali pulps will be considered. The first aspen pulp chosen for consideration was Pulp D, prepared from material fiberized similarly to the red maple material Y. Aspen fiberized materials O and P were selected because they were fiberized like red maple materials U and V, respectively. The selection of R will be discussed later. Each of these aspen materials was delignified using a three-step approach, namely lignin modification, alkali extraction, and hypochlorite reaction. This is the simplest chlorine dioxide-alkali approach to producing a bleached pulp. Data on the preparation of Pulps D, O, P, and R are given in Table XV.

It should be noted in connection with this table that the lignin modification time ranged from 180 to 295 minutes. This is believed to reflect a difference in the degree of subdivision of the fiberized material. The Bauer-McNett classification data in Tables IX and X do have differences that are compatible with this belief, although it would be difficult to predict the observed changes in reaction time from these classification data. Other points about the results in Table XV will be covered as the discussion proceeds.

CERTAIN OBSERVATIONS ON CHLORINE DIOXIDE-ALKALI PULPS

Effect of Bleaching

Pulps from V, Y, and U in Table XIII were beaten in a Valley beater and handsheet data obtained as in Appendix VI. A significant early observation revealed that for Pulps Vu and Vb:

with bleaching there was no decrease in the time taken to beat and handsheet densities were not significantly confined to the higher density range, as illustrated by Fig. 20.

TABLE XV

PREPARATION OF ASPEN CHLORINE DIOXIDE-ALKALI PULPS D, O, P, and R FROM FIBERIZED CHIPS

Ref.	ClO_2, %	NaOH, %	Avail. Cl_2, %	Time, min.	Final pH	Yield, %	Rejects, % o.d.p.	Klason + Acid-sol. Lignin, %	TAPPI Brightness Ethanol	TAPPI Brightness Water	Screening Loss, %
Lignin Modification[a]: Consistency 6.0%; temp. 25-35°C.											
D	9	3.5	-	295	2.6	95	-	-	-	-	
O	9	3.5	-	220	2.8	n.d.[b]	-	-	-	-	
P	9	3.5	-	210	2.7	n.d.	-	-	-	-	
R	9	3.5	-	180	2.5	n.d.	-	-	-	-	
Alkali Extraction[c]: Consistency 8.0%; temp. 60°C.											
D	-	9.0	-	120	11.7	68	-	5.6	-	-	
O	-	9.0	-	120	11.6	n.d.	-	n.d.	-	-	
P	-	9.0	-	120	11.5	n.d.	-	n.d.	-	-	
R	-	9.0	-	120	11.6	n.d.	-	n.d.	-	-	
Hypochlorite Reaction[c]: Consistency 12%; temp. 40°C.											
D	-	0.25	4.5	235	7.9	66	4.4	3.0[d]	n.d.	77[e]	n.d.
O	-	0.25	4.5	180	8.3	66	0.3	2.2	84	79[f]	1.4[g]
P	-	0.25	4.5	190	8.0	67	0.2	3.7	81	76[f]	0.9[g]
R	-	0.25	4.5	180	8.2	67	1.0	3.1	n.d.	76[f]	0.7[g]

[a] Deionized tap water used throughout except where noted.

[b] n.d. = not determined.

[c] Product soaked in sulfurous acid (pH 3.5-4) for 30 min. at 25°C.

[d] Data are for screen accepts for all pulps.

[e] Screened using tap water without recycling water.

[f] Screened using distilled water without recycling.

[g] Determined as described in experimental part.
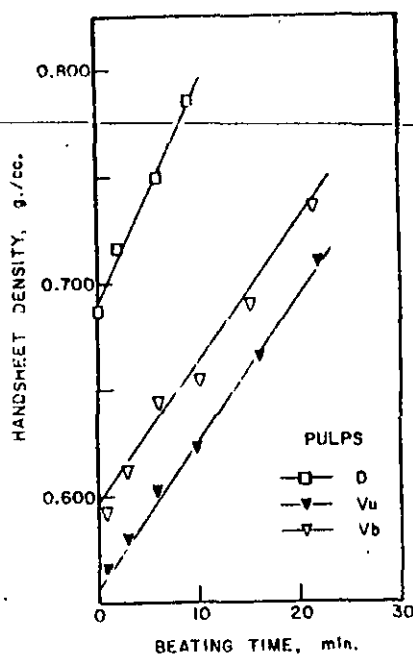
Figure 20. Initial Observations on Beating Time vs. Handsheet Density
for Red Maple Chlorine Dioxide-Alkali Pulps Vu and Vb
Compared with Aspen Pulp D

Furthermore, the lignin content and brightness of Pulp Vb are comparable to those

of aspen Pulp D, for example, and therefore it has now been demonstrated that:

lignin removal in chlorine dioxide-alkali pulps does not necessarily

lead to bleached fibers that behave like holocellulose fibers.

Influence of Changing Fiberization Equipment

In considering whether the above statement is related to species and/or

process, Pulps Yu and Yb are of particular interest for two reasons. Firstly,

the red maple fiberized material Y was prepared using essentially the same

conditions as those used to fiberize aspen chips for the preparation of Pulp D.

Secondly, Pulps Yu and Yb were delignified similarly to Pulps Vu and Vb.

The unbleached and bleached pulps from Y had beating time vs. handsheet density relationships as in Fig. 21 which are almost coincident with those for the unbleached and bleached Pulps B and D, respectively, prepared from identically fiberized chips. Because of a similarity in trend, the differences on the one hand between Pulp D and Pulps Vu or Vb and on the other hand between Pulp Yb and Pulps Vu or Vb, appear process dependent rather than species dependent.
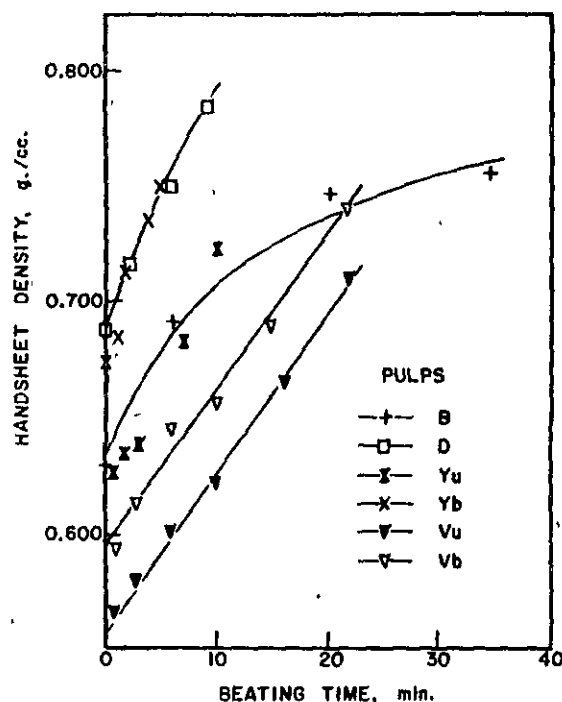
Figure 21. Beating Time vs. Handsheet Density Curves Revealing Process-Dependent Differences in Aspen Pulps B and D Compared with Red Maple Pulps Yu, Yb, Vu, and Vb

Since V and Y were delignified similarly, process-derived differences between them should relate to fiberization. This involved both a change of equipment and change of other fiberization conditions, including temperature. The conditions for fiberizing aspen and red maple in an OVP Asplund machine, as set out in Tables X and XI, do not include any careful simulation of the S185

Bauer fiberization conditions.   Thus, it is not possible to isolate mechanical factors or what is simply the effect of a change of equipment on the basis of information in hand.

Divergence from Trends for Chlorite-Alkali Pulps

From the results given in Table XII it is known that changes in fiberization conditions when using the same equipment can result in significant differences in delignified pulp properties.   Furthermore, for chlorite-alkali Pulps Sc and Tc and Uc and Vc, in each pair the pulp prepared from chips fiberized after a shorter time at either 133 or 158°C. gave a lower initial handsheet density and greater density range for handsheet drainage times of up to, say, 14 sec. (Fig. 18).   By analogy, it would be expected that evaluation of a chlorine dioxide-alkali pulp from U would lead to curves falling outside the area bounded by the y-axis and the curve for Pulp Vb in Fig. 20.   However, when U was chlorine dioxide-alkali delignified and evaluated similarly to pulps from V and Y (Table XIII and Appendix VI) the curve for Pulp Ub as shown in Fig. 22 had a position different from that expected.
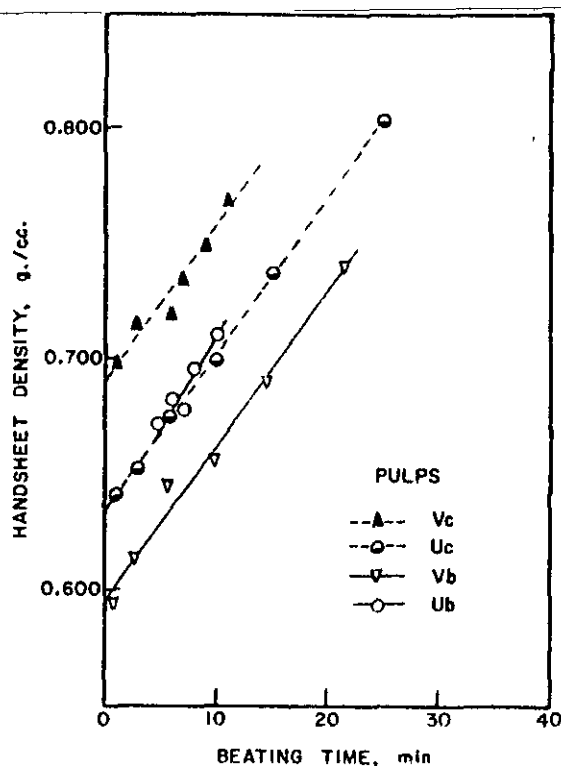
Figure 22. Beating Time vs. Handsheet Density Curves Revealing Different Trends
in Red Maple Chlorite-Alkali (Uc and Vc) vs. Chlorine Dioxide-Alkali
(Ub and Vb) Pulps

In Table XVI, handsheet drainage times are included with beating time

and handsheet density data for Pulps Uc, Vc, Ub, and Vb.   These again illustrate

the difference in the trends for the chlorine-alkali and chlorine dioxide-alkali

pulps.   The table also includes data from the preparation and evaluation of

chlorine dioxide-alkali Pulps Su and Tu (Tables XIII and Appendix VI).   These

likewise behave differently from the corresponding chlorite-alkali pulps.   Pulp

Sc beat more slowly than Pulp Tc, derived from chips fiberized at the same

temperature but after heating for a longer time.   For the chlorine dioxide-

alkali Pulps Su and Tu there is no similar trend.

TABLE XVI

COMPARISON OF CHLORITE-ALKALI AND CHLORINE DIOXIDE-ALKALI PULPS FROM RED MAPLE

	Chlorite-Alkali			Chlorine Dioxide-Alkali		
Pulp code		Uc			Ub	
Beating time, min.	1	6	15	1	3	5
Handsheet drainage time, sec.	4.7	4.8	7.3	5.1	6.3	8.1
Handsheet density, g./cc.	0.641	0.676	0.738	0.684	0.696	0.710
Pulp code		Vc			Vb	
Beating time, min.	1	6	11	1	6	22
Handsheet drainage time, sec.	5.3	7.4	14.6	4.7	4.8	11.5
Handsheet density, g./cc.	0.697	0.719	0.768	0.594	0.644	0.739
Pulp code		Sc			Su	
Beating time, min.	1	6	15	1	4	6
Handsheet drainage time, sec.	4.5	5.2	13.6	5.7	6.7	10.7
Handsheet density, g./cc.	0.614	0.676	0.755	0.595	0.637	0.687
Pulp code		Tc			Tu	
Beating time, min.	1	4	8	1	5	7
Handsheet drainage time, sec.	6.0	7.8	13.0	6.0	9.6	14.6
Handsheet density, g./cc.	0.742	0.755	0.788	0.599	0.641	0.668

It is concluded that at present it is unclear how the results for chlorite-alkali pulps can be used on a broad basis to predict the papermaking properties of chlorine dioxide-alkali pulps.

TRENDS FOR RED MAPLE AND ASPEN CHLORINE DIOXIDE-ALKALI PULPS

Selection of Pulps for Comparison

An outcome of the discussion above on Fig. 21 was that the differences illustrated for red maple and aspen pulps in Fig. 20 are process dependent rather than species dependent. More particularly, the process-derived differences are related to fiberization conditions.

This conclusion will now be examined more fully by broader consideration of chlorine dioxide-alkali pulps from red maple and aspen. Pulps from the red maple fiberized materials V, Y, and U have been selected for comparison with pulps from the aspen fiberized materials P, D, and O. These six materials can be regarded as three pairs, namely V and P, Y and D, plus U and O. The first and last pair were obtained using the OVP Asplund machine with the same conditions of fiberization for each pair, but chips corresponding to the last pair were heated for a shorter time. The other pair (Y and D) was obtained using the S185 Bauer machine with the same conditions of fiberization for each member of the pair.

By this selection, the following position is reached. If, from changes in the conditions of fiberization, when using only one machine, pulps are prepared with a spread of properties similar to that obtained when using different machines, this would provide evidence indicating mechanical factors such as plate pattern or the use of a single-disk vs. double-disk machine are not the basis of the observed differences in pulp behavior.

Comparison of Handsheet Data

To facilitate comparison of the handsheet data for red maple and aspen in Appendices VI and VII, pairs of graphs have been plotted as in the figures below:

> Figure 23. Beating Time vs. Handsheet Drainage Time
>
> Figure 24. Beating Time vs. Handsheet Density
>
> Figure 25. Beating Time vs. Breaking Length
>
> Figure 26. Beating Time vs. Tensile Energy Absorption
>
> Figure 27. Beating Time vs. Burst Factor
>
> Figure 28. Beating Time vs. Tear Factor x Yield/65
>
> Figure 29. Beating Time vs. M.I.T. Fold

When Fig. 23-29 are considered as one group, a unique characteristic is that, excepting Fig. 23 and 28 for the moment, the pattern of curves in each figure is remarkably similar.   The pattern seen reflects the relative positions of the beating time vs. handsheet density curves in Fig. 24.

Although handsheet drainage time data are not available for Pulp D, it is known from Fig. 4 that its drainage resistance increased relatively rapidly as beating proceeded for 10 minutes.   Thus, if handsheet drainage time data had been obtained it seems likely the curve would have an appreciably steeper slope than that of either Pulp P or O in Fig. 23.   This would mean the relative positions of the curves in Fig. 23 would be similar to those in Fig. 24.

Figure 28 seems different only in that tear factor decreases, as usual for hardwoods, with beating time whereas other properties as in Fig. 23-27 increase. When this is taken into account, the relative positions of the tear factor curves correspond to those for handsheet density.
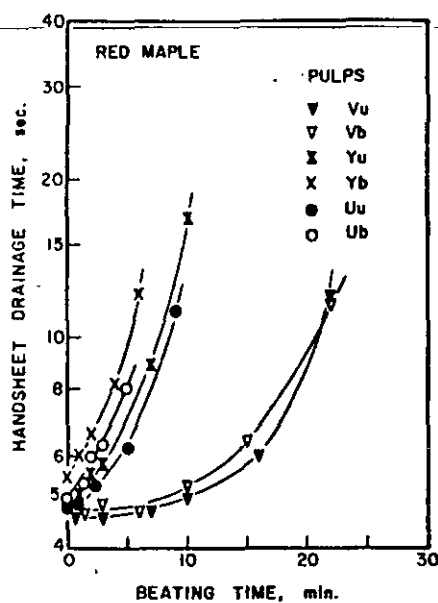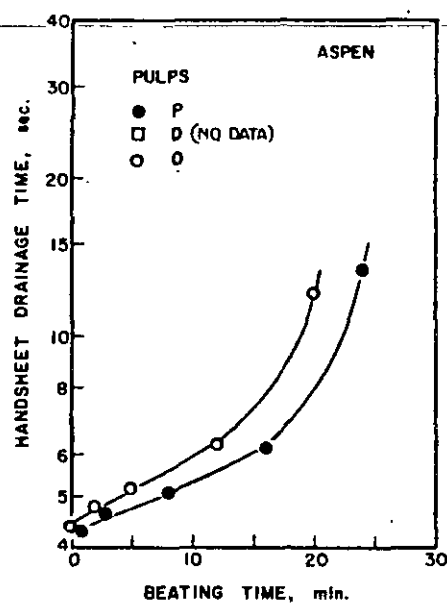
Figure 23. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing Beating Time vs. Handsheet Drainage Time

Figure 24. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing Beating Time vs. Handsheet Density

Figure 25. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing
Beating Time vs. Breaking Length

Figure 26. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing
Beating Time vs. Tensile Energy Absorption

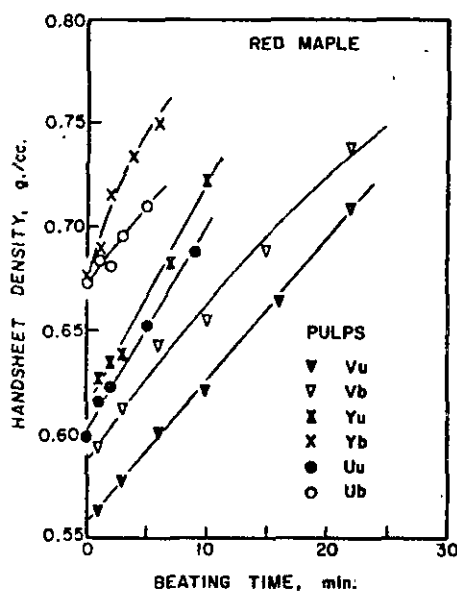Figure 27. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing
Beating Time vs. Burst Factor

Figure 28. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing
Beating Time vs. Tear Factor x Yield/65
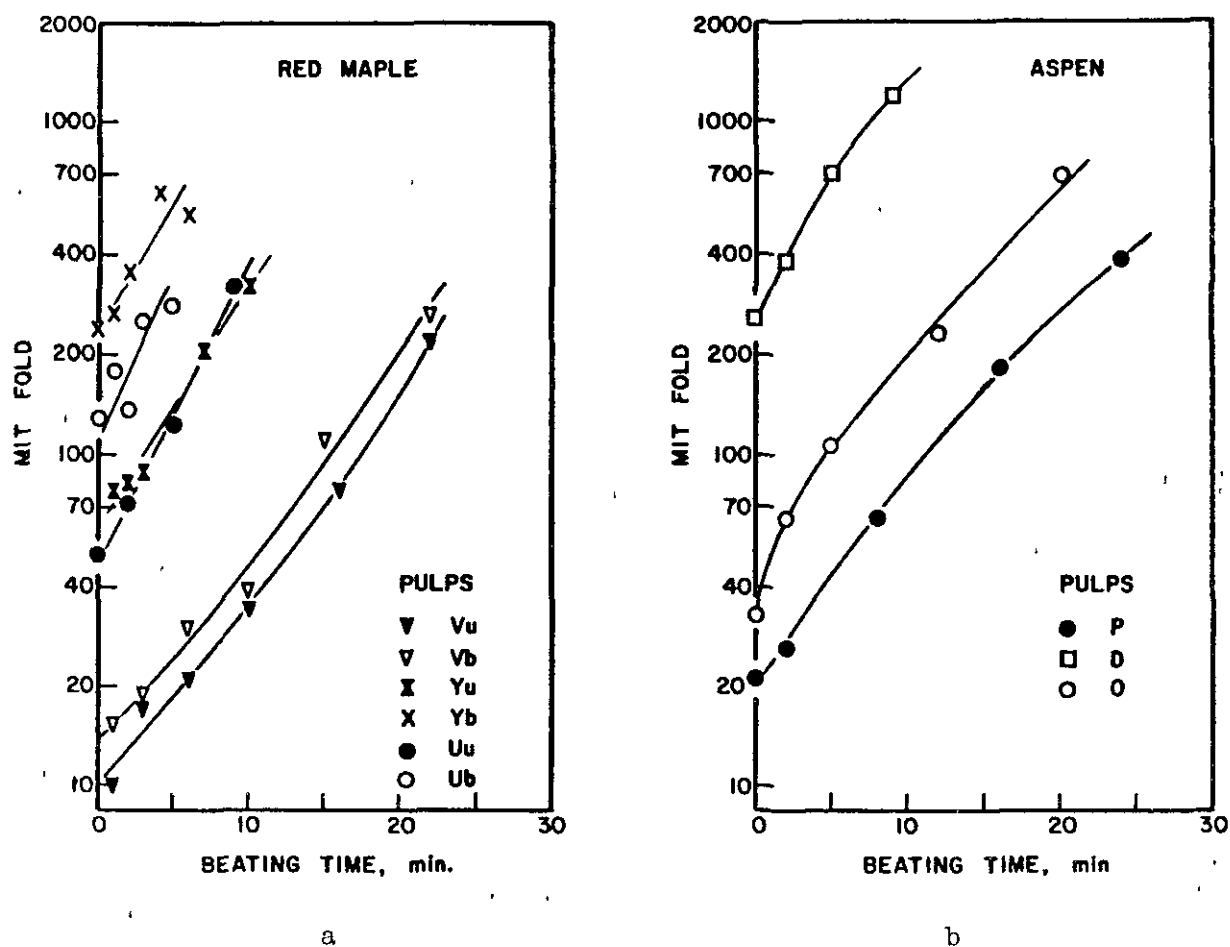
Figure 29. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing
Beating Time vs. M.I.T. Fold

Not all of the handsheet properties fitted into the above pattern, as can be seen from the results presented in Fig. 30-33.

It appears that a lesser dependence on sheet density distinguishes the group of results for tensile stiffness, zero-span breaking length, smoothness, and specific scattering coefficient, as in Fig. 30-33, respectively, from the group of results in Fig. 24-29. On this basis, the group of results in Fig. 30-33 does not appear anomalous.

The results in Fig. 31 for zero-span breaking length proved to be surprising in that aspen fiberized in the IPC S185 Bauer, compared with the Asplund machine, led to a pulp with greater zero-span breaking length (Pulp D compared with Pulps O and P), whereas red maple fiberized in the Bauer machine led to a pulp with relatively lower zero-span breaking length before bleaching (Pulp Yu compared with that from U V). This difference is apparently related to species.

Smoothness results in Fig. 32 indicate that, at the same handsheet density, better shive reduction or separation of fiber bundles resulted when fiberization was carried out under the conditions used with the Asplund machine.

There also appears to be a species-related difference in the results obtained for specific scattering coefficient data as illustrated in Fig. 33. The spread in the data for red maple is particularly marked. Since it is generally accepted that light scattering is mainly dependent on the unbonded surface area of fibers, variation in specific scattering coefficient would be expected to reflect variation in a bonding-dependent property like breaking length. As this increases as a specific pulp is beaten, light scattering decreases. The breaking length data in Fig. 25 are essentially in accord with the data in Fig. 33. Those red maple pulps related to the curves with highest specific scattering coefficients
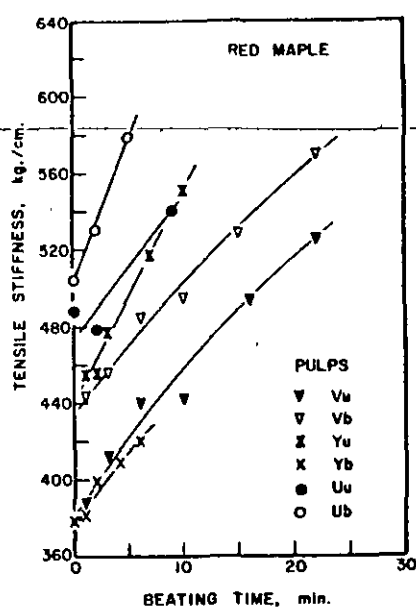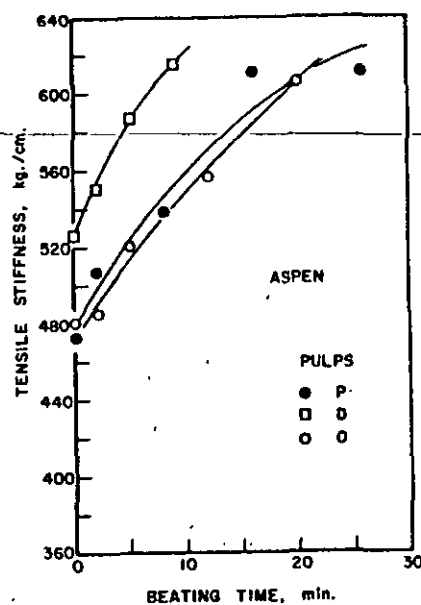
Figure 30. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing
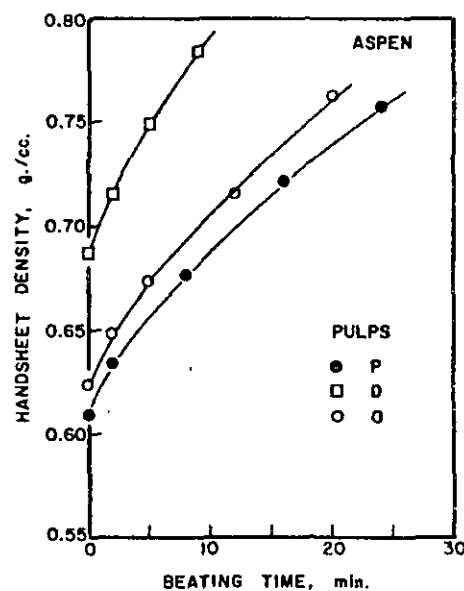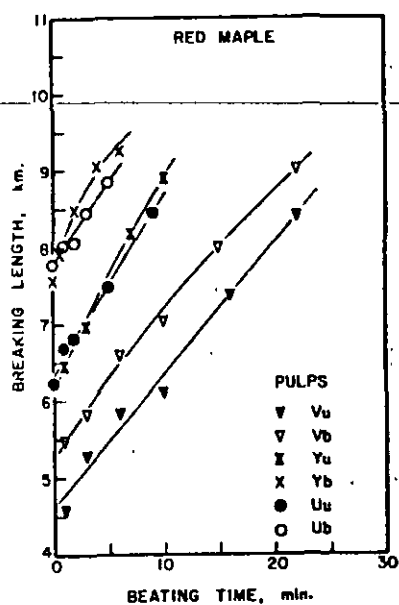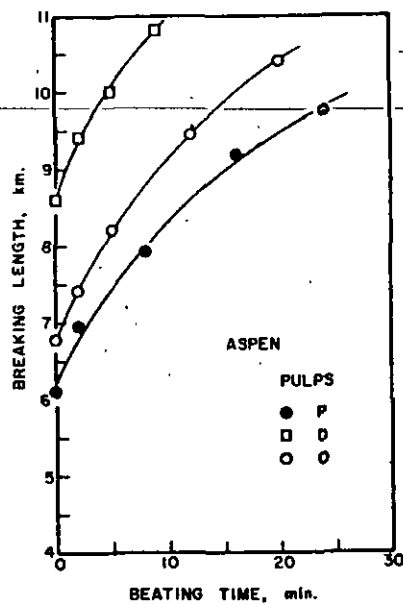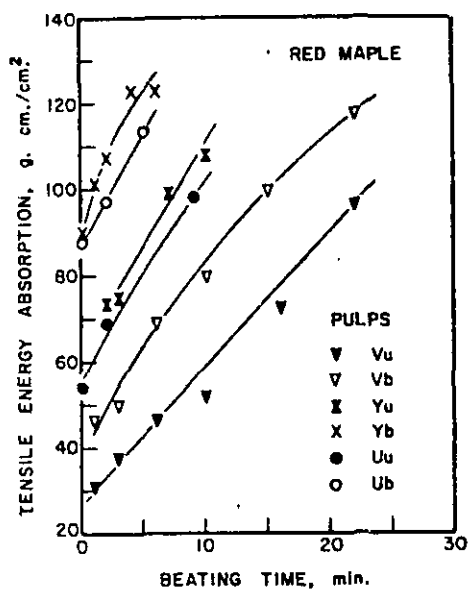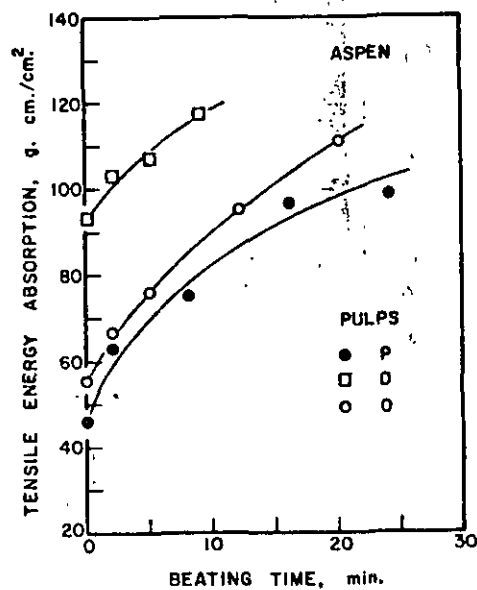Beating Time vs. Tensile Stiffness
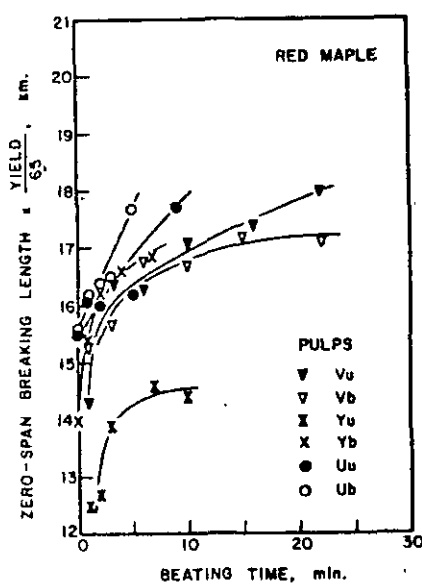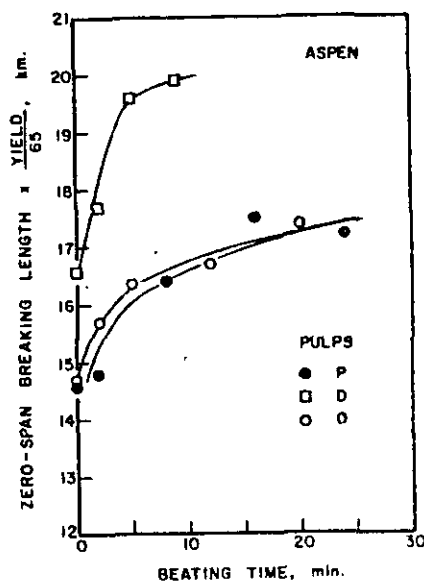
Figure 31. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing
Beating Time vs. Zero-Span Breaking Length
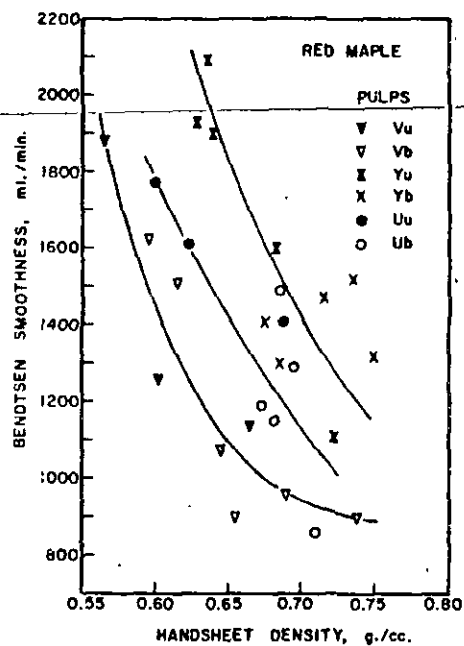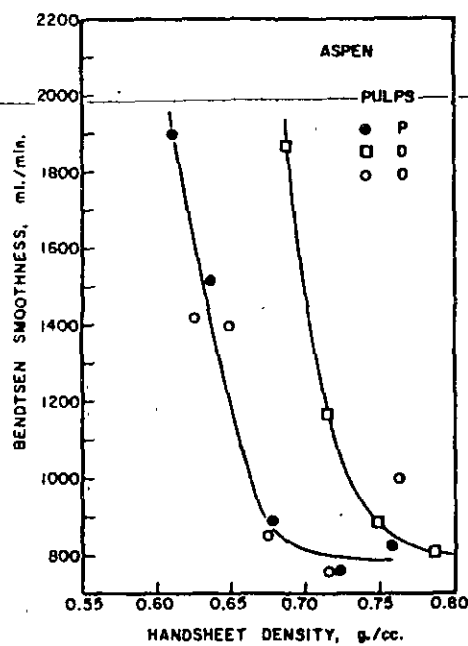
Figure 32. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing Handsheet Density vs. Smoothness
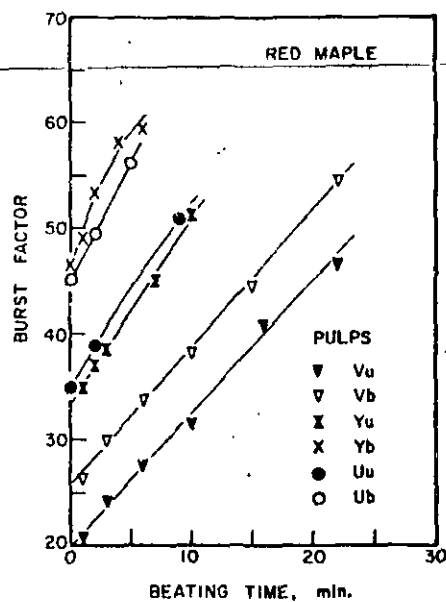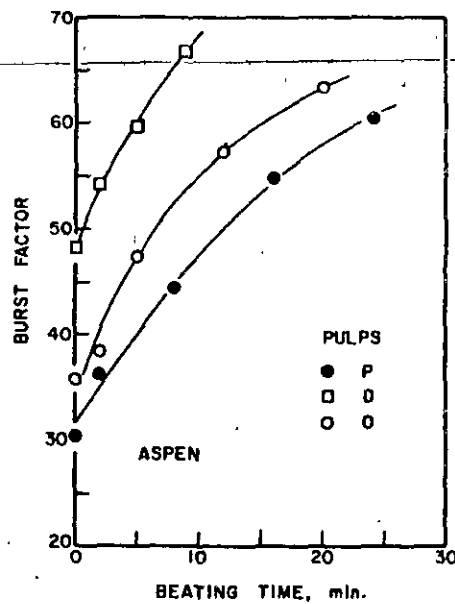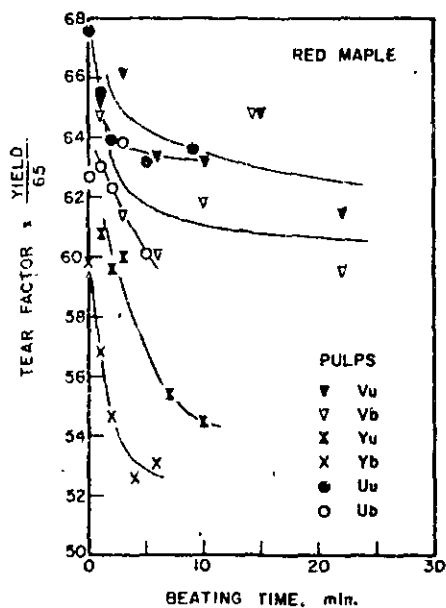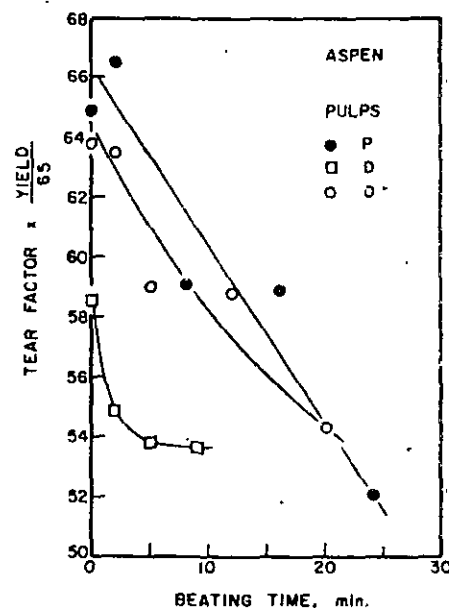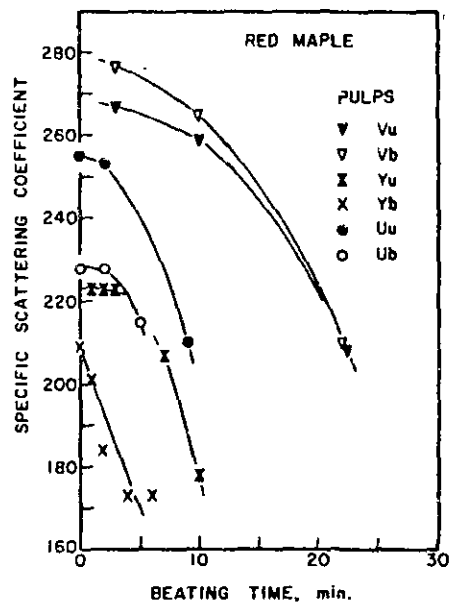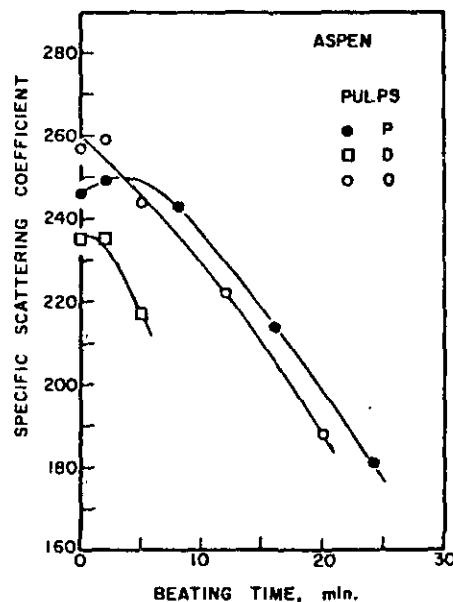

Figure 33. Red Maple (a) and Aspen (b) Chlorine Dioxide-Alkali Pulps Showing Beating Time vs. Specific Scattering Coefficient

correspond to those with lowest breaking length and vice versa. A similar trend applies to aspen. However, it appears from Fig. 33 that the red maple handsheets as a group cover a greater range of unbonded surface area than the aspen group. Maximum unbonded surface area seems to be associated with the case where red maple pulps were derived from chips fiberized under conditions used with the Asplund machine, i.e., for pulps from U and V. The marked difference between the upper and lower curves for red maple specific scattering coefficient data in Fig. 33 is believed to relate in part to a difference in the extent of separation into individual fibers. This is supported by the observation that at equal breaking length, or at comparable bonding, light-scattering data are greater in relation to Pulp Vb compared with Pulp Yb (Table XXIV in Appendix VI).

To consider what is the origin of the pattern observed in Fig. 23-29, Fig. 24 may be regarded as representing the whole set. It will be seen that extreme differences in behavior of the various pulps in this figure are associated with the two pairs of fiberized materials V and P plus Y and D, obtained using the OVP Asplund and S185 Bauer machines, respectively, with between-pair differences in conditions of fiberization but the same within-pair differences. Because the extreme differences in behavior of the red maple and aspen pulps follow changes in fiberization, this broadens the basis for concluding these differences are related to fiberization conditions.

Fiberization as a Factor in Pulp Behavior

Since the results obtained for Pulps Yu and Yb are very similar to those for Pulps Uu and Ub, the use of different machines for preparing the corresponding fiberized materials does not appear to have introduced some mechanical factor responsible for the differences in behavior of pulps derived from V and P compared with Y and D. If machine design, with matters such as plate pattern and disk

mechanics in mind, is not an aspect of fiberization responsible for the extreme

differences between the red maple and aspen pulps, then some other aspects of

fiberization must be involved.   These will be considered first by looking at the

case of red maple.

At this point, the differences in behavior of the red maple pulps derived

from U and V might logically be explained as follows.   Because the only difference

in the preparation of pulps from U and V is a longer time at temperature for V

before fiberization, it might be concluded there was insufficient time in the case

of U for the chips to become heated to temperature.   While this is conceivable,

other data do not clearly support this thought.

For example, the analogy between fiberization conditions and relative

position of the curves based on handsheet data for red maple is not completely

paralleled by aspen (Fig. 23-29).   In the case of pulps derived from the pair of

identically fiberized materials U and O, pulps from O have curves positioned near

those associated with P, whereas pulps from U have curves positioned nearer to those

associated with Y instead of V.   In other words, although the extreme differences

in behavior of the red maple and aspen pulps in Fig. 23-29 are associated with the

two pairs of fiberized materials V and P plus Y and D, the results for the other

matched pair of fiberized materials lie closest to those associated with P and Y,

respectively, instead of either V and P or Y and D.

A second example indicative of the fact that the differences observed in

the red maple pulps from U and V are not a simple matter of time at temperature is

found in the results obtained for the red maple pulps from S and T.   This pair of

fiberized materials differed from the other pair (U and V) only in regard to

fiberization temperature.   For S and T the temperature was 133°C. compared with

158°C. for U and V (Table XI).   On this basis, it might be expected that evaluation

of chlorine dioxide-alkali Pulps Su and Tu (Table XIII) would reveal significant differences as had been found for Pulps Uu and Vu. This was not found to be the case. Evaluation gave handsheet data showing no marked differences between Pulps Su and Tu (Appendix VI).

In addition to Pulp Su being similar to Pulp Tu, it was found that Pulps Tu and Tb behaved more like pulps from Y or U than from V, although a similarity between pulps from T and V might be expected if equal time at temperature had been critical during fiberization.

The dissimilarity of handsheet data for Pulps Tu and Tb compared with Pulps Vu and Vb is illustrated in Fig. 34 and 35. As for the case of Fig. 23-29 discussed above, breaking length and tear factor data reflect the relative positions of the beating time vs. handsheet density curves.

It is interesting to note that zero-span breaking length data in Fig. 36 (a) reveal no obvious differences in fiber strength of pulps from T compared with V. However, the existence of a significant difference in the nature of pulps from T and V is confirmed by the very marked differences in specific scattering coefficient data shown in Fig. 36 (b) and Appendix VI.

There is no indication given by the Bauer-McNett classification data in Table XI that the higher sheet density, higher breaking length, and lower specific scattering coefficient data for Pulps Tu and Tb compared with Pulps Vu and Vb are related, for example, to finer material being produced during chip fiberization. Nevertheless, in view of the more desirable papermaking properties that characterize Pulps Vu and Vb, it would be of considerable interest to understand why the particular conditions used in chip fiberization to prepare V have given improved properties.
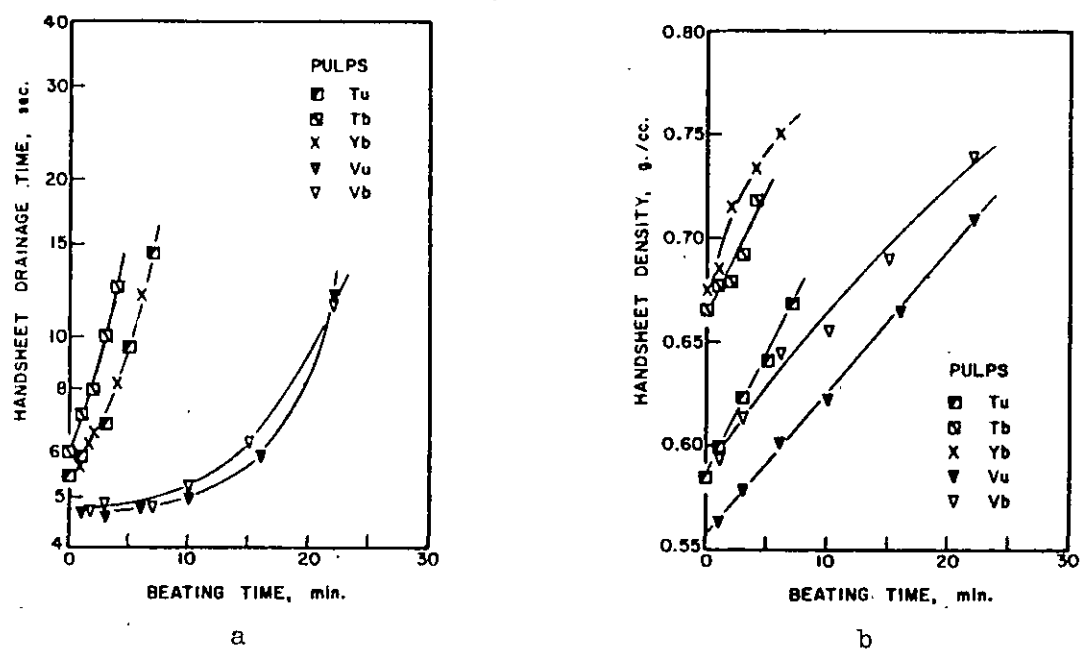
Figure 34. Red Maple Chlorine Dioxide-Alkali Pulps Showing Beating Time vs. Handsheet Drainage Time (a) and Handsheet Density (b)
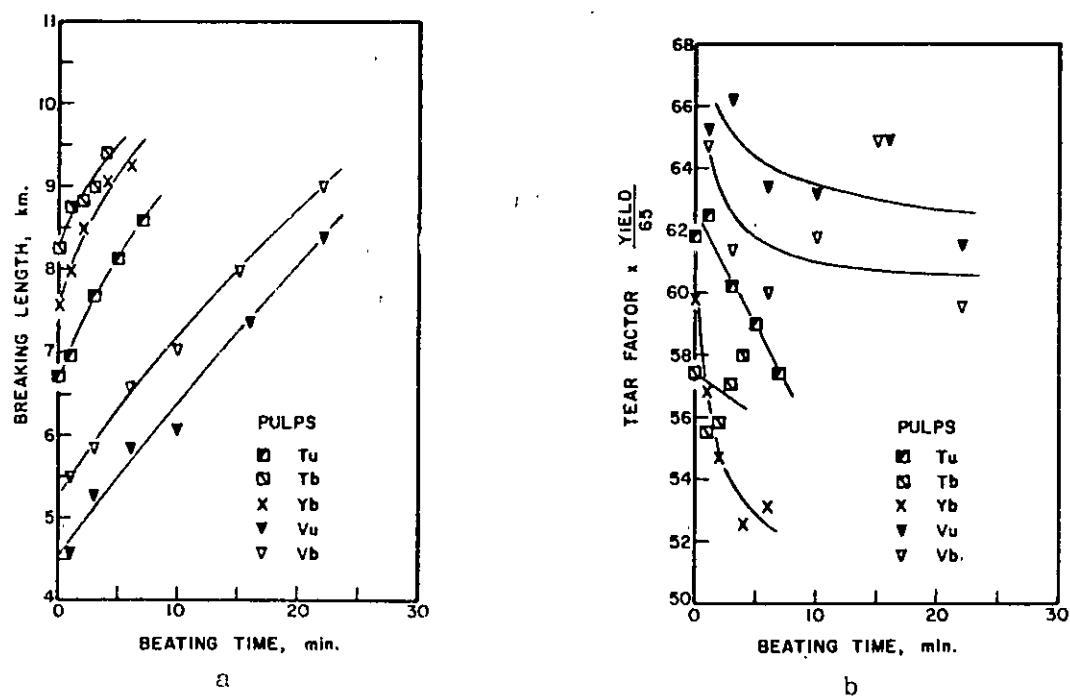
Figure 35. Red Maple Chlorine Dioxide-Alkali Pulps Showing Beating Time vs. Breaking Length (a) and Tear Factor x Yield/65 (b)

a

b
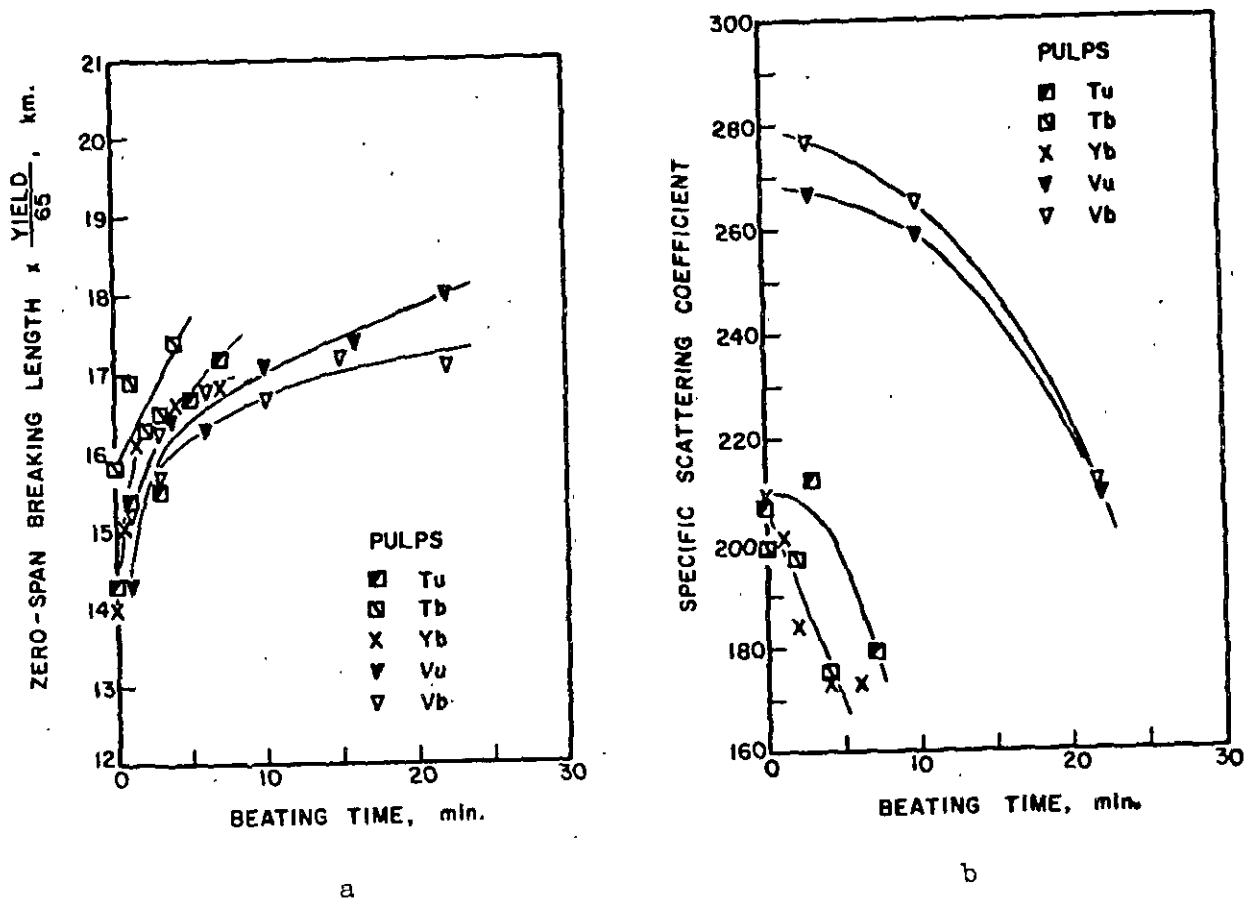
Figure 36. Red Maple Chlorine Dioxide-Alkali Pulps Showing Beating Time vs.
Zero-Span. Breaking Length (a) and Specific Scattering Coefficient (b)

IMPROVED CHLORINE DIOXIDE-ALKALI PULP PROPERTIES

General Consideration

On the basis of the investigations discussed above it has been concluded

that the improved properties of the red maple and aspen chlorine dioxide-alkali

pulps from the similarly fiberized materials V and P are temperature dependent and,

at least in the case of red maple, time dependent with respect to the chip fiberiza-

tion step.

Since elevated pressures are needed to achieve the temperature applicable

to the preparation of V and P, this must be taken into account in machine design,

but apart from this no evidence has been obtained that other mechanical factors,

such as plate pattern and so on, are critical. Therefore, the explanation for the

observed improvements in the chlorine dioxide-alkali pulps must rest in some aspect

of the physical and/or chemical changes that could occur during the fiberization

process. Conceivably, there could be factors of relevance that are common to hard-

woods in general, and other factors more related to species.

A common phenomenon that could possibly distinguish chlorine dioxide-

alkali pulps based on V and P from those based on S, T, U, Y, and D is chip plasti-

cization. This suggestion is compatible with the observations made on the fiberized

materials as discussed in connection with Fig. 14-16 and Tables X-XI.

Originally, thoughts associated with degree of plasticization being

important to pulp properties were focused on factors such as fiber damage, as

reflected by across-fiber breaks and a reduction in zero-span breaking length.

Fiber length distribution data, as in Fig. 16, and zero-span breaking length curves,

as in Fig. 31 and 36(a), provide no clear indication of significant changes related

to the pattern of curves in Fig. 23-29, for example.

The general question of what specific changes have caused the chlorine dioxide pulps based on V and P to have more desirable papermaking properties seems to resolve itself into alternative questions. These are concerned with either an explanation for the differences in handsheet density shown in Fig. 24 and/or an explanation for the differences in handsheet drainage time shown in Fig. 23 that is some function of the time/temperature conditions applicable to the fiberization step.

Observations on Hydrodynamic Properties

To obtain data on the hydrodynamic properties of the pulps represented in Fig. 24, for example, it would be necessary to repeat most of that work. However, some information on hydrodynamic properties has been obtained for aspen Pulp R (Table XV), handsheet data on which are included in Appendix VIII.

Information is also available on the hydrodynamic properties of Pulp D. Hence, these properties can be considered for two pulps prepared with a similar delignification procedure (Table XV), but using different time and temperature conditions in the fiberization step (Tables X and XIV). In addition, these pulps had different beating characteristics in that Pulp R gave somewhat lower density handsheets (Appendix VIII).

Hydrodynamic properties of Pulps D and R are included in Table XVII. It is recognized that this information is limited, but in view of its potential value in understanding the differences in papermaking properties that originate in the fiberization step of the process, some discussion seems appropriate.

TABLE XVII

HYDRODYNAMIC PROPERTIES OF ASPEN PULPS D AND R

Pulp	D		R	
Beating time, min.	2	9	9	18
Drainage resistance, $\underline{R} \times 10^{-8}$ cm./g., $\Delta\underline{P} = 10$ cm. H_2O	1.09	2.20	1.70	4.69
Specific surface, $<\overline{\underline{S}}_w>$, cm.^{2}/g.	18,400	29,300	23,900	41,000
Specific volume, $<\overline{\underline{v}}>$, cc./g.	2.99	3.34	3.49	3.59
Compressibility, $\underline{c} = \underline{M}\underline{P}^{\underline{N}}$				
$\underline{N}$	0.392	0.435	0.414	0.414
$\underline{M} \times 10^{-2}$	0.156	0.091	0.119	0.122
Handsheet density, g./cc.	0.716	0.784	0.717	0.801

Apparently, Pulp D differs from Pulp R in that the former has significantly more specific surface without a significant difference in specific volume after beating for 9 min. This results in Pulp D having a greater drainage resistance than Pulp R after an equal amount of beating.

The compressibility data are also of particular interest. When the compressibility equation is written in the form

$$\log C = N \log P + \log M$$

changes in $d(\log \underline{C})/d(\log \underline{P})$ are indicated by changes in $\underline{N}$. Normally when, for example, a given kraft pulp is beaten, $\underline{N}$ remains constant. Pulp D is unusual in that $\underline{N}$ has increased during the beating process, indicating a greater increase in $\log \underline{C}$ for a given increase in $\log \underline{P}$. On the other hand, for Pulp R, $\underline{N}$ remained constant, or as beating proceeded there was no change in $d(\log \underline{C})/d(\log \underline{P})$, as applies to a kraft pulp.

Suggested Basis for Observed Differences in Pulp Properties

The above tends to indicate Pulp D is being unusually changed by the beating process and it appears there could be an internal weakening of the fiber structure which is not paralleled in Pulp R.   This change is consistent with the greater specific surface found for Pulp D after beating for 9 min.

The differences observed for a fraction of red maple fiberized chips T and V in Fig. 14 also indicate a greater degree of disruption of the individual fiber structure had occurred in T which was fiberized at 133 compared with 158°C. for V, after equal time at temperature.

Thus, it is suggested that aspen and red maple fibers could have an inherently greater degree of internal strength when chip fiberization is carried out after heating for 4-6 min. at 158°C. and this leads to pulps with more desirable papermaking properties.

It is conceivable that the span of optimum time and temperature for heating chips before fiberization varies to some extent with species.   This could explain the incomplete parallel between fiberization conditions and relative position of the curves based on handsheet data for red maple and aspen (Fig. 23-29) pointed out earlier in this discussion.   In fact, the direction of the observed differences for aspen compared with red maple is in accord with the knowledge that increased moisture content facilitates plasticization.   Because of aspen's lower density, the chips had a moisture content of 67-69% when fiberized compared with 57-60% for red maple chips (Tables X and XI).

If it is imagined that lignin removal causes a decrease in internal bonding of fiberized chips and if fiberization is not all in the compound middle lamella, formation of additional surface on beating would be facilitated by:

(a) increased lignin removal, and

(b) fewer clean breaks in the compound middle lamella.

IMPLICATIONS OF CHIP FIBERIZATION STUDY

Comparison of Chlorine Dioxide-Alkali Pulp Properties

A comparative summary of the results obtained for chlorine dioxide-alkali

pulps from differently fiberized chips of aspen and red maple is given in Table

XVIII.   More complete details are recorded in Tables X, XI, XIII, XIV, XV, and

Appendices VI and VII.

From this table it will be seen that each species of wood had been

fiberized using conditions differing with respect to machine and fiberization

temperature.   For aspen these different materials were similarly delignified with

the inclusion of a one-stage chlorine dioxide reaction.   The red maple materials

also were similarly delignified but with the inclusion of a two-stage chlorine

dioxide reaction and the chlorine dioxide contained a significant amount of chlorine.

A reduction in screen rejects and an increase in specific scattering

coefficient is seen in the pulp data for both species when fiberized at a higher

temperature.   This also led to longer beating times and a greater handsheet density

range.

Handsheets at 0.69 g./cc. were smoother and stiffer for both species when

fiberized at a higher temperature, and specific scattering coefficient was signifi-

cantly greater in the case of red maple.

TABLE XVIII

COMPARISON OF RESULTS FOR CHLORINE DIOXIDE-ALKALI PULPS FROM
DIFFERENTLY FIBERIZED CHIPS OF ASPEN AND RED MAPLE

Wood	aspen		red maple	
Fiberization				
Machine	IPC Bauer	OVP Asplund	IPC Bauer	OVP Asplund
Fiberization temp., °C.	≈100	158	≈100	158
Delignification				
Alkali conditioning	none	none	yes	yes
Number of aq. ClO_2 stages	one	one	two	two
Alkali extraction, °C.	60	60	70	70
Hypochlorite reaction	yes	yes	yes	yes
Chemical addition				
Chlorine dioxide (chlorine), %	9.0	9.0	7.5(1.3)	7.5(1.3)
Sodium hydroxide, %	12.75	12.75	10	10
Sodium hypo., % avail. Cl_2	4.5	4.5	3.0	3.0
Pulp data				
Total yield, %	66	67	64	66
Screen rejects, %	4.4	0.2	6.2	3.8
Klason + acid-sol. lignin, %	3.0	3.7	3.3	2.9
TAPPI brightness (water)	77	76	80	81
Spec. scattering coefficient	235	246	≈210	≈270
Valley beater evaluation				
Beating time, min.	9	24	6	22
Density range, g./cc.	0.69-0.78	0.61-0.76	0.68-0.75	0.59-0.74
Handsheet properties at 0.69 g./cc.				
Bendtsen smoothness, ml./min.	1700	800	1400	910
Spec. scattering coeff., 650 nm.	240	240	200	250
Breaking length, km.	8.7	8.2	8.1	7.9
Stretch, %	2.6	2.4	3.0	2.8
Tensile stiffness, $\underline{Et}$, kg./cm.	530	560	390	530
Burst factor	49	48	50	45
Tear factor	57	58	58	61

Significant Observations

In broadening the base of chip fiberization conditions studied, some
significant observations can be made with respect to the position reached previously.
These are:

(a) The fibrous raw material has been expanded to include red maple
     with success.

(b) For both aspen and red maple a bleached chlorine dioxide-alkali
     pulp has now been obtained that is capable of being beaten without
     handsheet drainage time increasing as rapidly as before.

(c) For both species bleached pulp handsheets have been prepared with
     a greater density range that includes appreciably lower densities
     than obtained before from a comparably bright pulp.

(d) For both species and coinciding with (b) and (c) the incidence of
     persistent shives has been noticeably reduced at a particular
     handsheet density as indicated by smoothness.

(e) For both species the relevant steam pressure and time of retention
     at that pressure during chip fiberization influence the papermaking
     properties of pulps and call for the use of a machine designed to
     operate above atmospheric pressures to achieve the improved results
     as above.

ASSESSMENT OF HARDWOOD CHLORINE DIOXIDE-ALKALI PULPS

To gain some assessment of the potential usefulness of aspen and red maple
chlorine dioxide-alkali pulps, results obtained using chips fiberized at 158°C.

(Table XVIII) are compared with evaluation data for other pulps in Table XIX.

Complete details on the aspen and red maple kraft reference pulps are given in

Appendix IX.

TABLE XIX

COMPARISON OF CHLORINE DIOXIDE-ALKALI PULPS WITH OTHERS

Source	Aspen		Red Maple		Bagasse[a]
Process	holo.	kraft	holo.	kraft	
Bleached or unbleached	bl.	unbl.	bl.	unbl.	bl.
Total yield, %	67	50	66	52	n.a.
Beating time, min.[b]	24	24	22	28	12
Sheet density range, g./cc.	0.61-0.76	0.59-0.80	0.59-0.74	0.61-0.82	0.65-0.76
Density for handsheet properties, g./cc.			0.69		
Breaking length, km.	8.2	8.2	7.9	8.6	6.3
Stretch, %	2.4	2.2	2.8	1.9	2.7
Tensile stiffness, E_t, kg./cm.	560	560	530	610	435
Tear factor (Elmendorf)	58	79	61	73	56
Bendtsen smoothness, ml./min.	800	500	910	300	840
Spec. scattering coeff.	240	300	250	350	260

[a] Commercial bagasse pulp, evaluation data for which are given in Appendix X.

[b] Bedplate weight = 2.2 and 5.5 kg. for holo. and other pulps, respectively.

It will be seen from Table XIX that the aspen and red maple chlorine

dioxide-alkali pulps are produced in about 30% greater amount than the correspond-

ing kraft pulps. These holopulps are easier to beat than the kraft pulps, but

probably beat about like a bleached bagasse pulp.   Except for tear factor, smooth-
ness, and specific scattering coefficient, the handsheet properties at 0.69 g./cc.
sheet density approximate those for the corresponding kraft pulps.   Tear factor,
smoothness, and specific scattering coefficient data are more like those for a
commercial bleached bagasse pulp.   However, handsheets for this had a lower breaking
length and lower tensile stiffness than the hardwood chlorine dioxide-alkali pulps.

The data in Table XIX indicate it is feasible to produce desirable paper-
making chlorine dioxide-alkali pulps from hardwoods.

EXPERIMENTAL

RAW MATERIALS

Aspen

The chips were from four quaking aspen trees obtained from The Institute
of Paper Chemistry farm at Greenville, Wisconsin.   Twenty-foot logs were cut from
each tree and the butt diameters ranged from 5 to 6 inches and top diameters from
2 to 3 inches.   The logs, after being debarked, were chipped on a 4-knife, 38-inch
diameter Carthage chipper to give a nominal 5/8-inch chip.   The chips were screened
on a large 4-mesh screen with the through fraction being discarded and oversize
chips and knotty pieces being removed manually.   The screened chips were sealed in
plastic barrel liners and stored at 40°F.   They had a moisture content of 47% on a
wet basis.

Red Maple

Twelve logs of red maple, each 100 inches long with underbark diameters
ranging from 8 to 10 inches, were received from one of the sponsors during April,
1969.   Debarking and chipping were carried out as for the aspen logs and the chips
were screened through a 24-inch Sweco Dynoscreen with the through-1-in.-and-on-4-
mesh fraction being retained.   The screened chips were sealed in plastic barrel
liners and stored at 40°F.   They had a moisture content of 35.2% on a wet basis
and a density of 31.5 lb. (o.d.)/cu. ft. (green).

Pin Chips

Aspen pin chips were made by hand guillotining the screened chips into
matchstick-size "pins" of approximately 3/32 in. x 3/32 in. x 5/8 in.   Red maple
pin chips were made by guillotining 3/8-in. thick disks cut from the 12 logs into

approximately 3/32 in. x 3/32 in. x 3/4-in. pin chips.   Both lots of pin chips were

sealed in plastic bags and stored at 40°F.

FIBERIZING

S185 Bauer

Fiberized chips were prepared in the double-disk S185 Bauer at the I.P.C.

according to the procedure in Report Three, page 55, except that a more even feed

rate was used as referred to in Report Six, page 48.

OVP Asplund Defibrator

The equivalent to 100 lb. ovendry of both, aspen and red maple chips were

put into plastic-lined 50-gal. fiber drums and dispatched by air freight to AB

Defibrator, Stockholm, during May, 1969.   A small cloth bag containing thymol

crystals was placed in with each drum of chips.   Fiberizing of the aspen and red

maple chips was carried out in early June, 1969.   It was observed that the aspen

chips were noticeably stained and that the red maple chips were beginning to show

surface staining in some parts of the bags.

A diagram of equipment similar to that used in this work, together with

an illustration of the plate pattern used, is shown in Fig. 13.

Impregnation of the chips with water was carried out batchwise with the

equivalent of 5 kg. of moisture-free chips per batch.   The impregnator consisted

of a stainless steel digester with a close-fitting basket to hold the chips.

The preheater, defibrator, and blow tank were operated as one unit.

The preheater had a capacity of about 10 kg. dry weight of chips with a maximum

steaming pressure of 86 p.s.i.   All of the water-impregnated chips of a batch were

tipped into the preheater. After these chips were steamed under a given pressure for a selected time, they were continuously fed, without forming a chip plug, by a screen feed into the throat of a Type OVP Asplund defibrator at a feed rate equivalent to about 1 kg. moisture-free chips per minute. The defibrator had 20-in. diameter disks fitted with no. 5821 pattern plates. A single disk driven by a 110-h.p. motor rotated at 1500 r.p.m. corresponding to a peripheral speed of 130 ft. per second. The fiberized product was collected from the initial, middle, and final thirds of the feeding period. Details of the conditions of fiberization are given in Tables X and XI.

SODIUM CHLORITE-ALKALI DELIGNIFICATION

This is essentially a three-stage procedure consisting of an initial alkali conditioning, an acidified sodium chlorite oxidation, followed by an alkali extraction. The treatment has become standardized with the only variable being the sodium chlorite reaction time, which is governed by chip size and species. Usually the amount of fibrous starting material was equivalent to 800 g. ovendry. For the fiberized chips, all the reactions were carried out in plastic bags with dewatering being effected by a laundry spin drier using a nylon bag to contain the reacted products. For the pin chips, the reactions were carried out in a 10-liter glass vessel with dewatering being effected by simply draining the upturned vessel over a 3-liter sintered-glass filter funnel. Most of the pin chips would tend to "hang up" inside the glass vessel during the latter operation. During each of the reactions, the products were mixed or shaken at regular intervals.

Alkali Conditioning

The fiberized chips and the pin chips were treated with 10% sodium hydroxide, based on the ovendry fibrous material, at a pulp consistency of 10%.

The temperature was raised from ambient to 50°C. in 45 min. and held at 50°C. for 60 minutes.   Before heating the pin chips, they were given a 15-minute vacuum treatment.   After the reaction time had been completed, the product was washed three times with deionized water, then soaked in an acetic acid solution (4.5% acetic acid on the ovendry weight of original fibrous material) for 2 hours at room temperature, then washed four times with deionized water.

Sodium Chlorite Oxidation

The alkali-conditioned product was treated with 100% sodium chlorite and 15% acetic acid at a 10% pulp consistency.   Both chemical percentages are based on the original ovendry starting material.   The reaction started out at room temperature, but the mixture self-heated up to about 40°C. in four hours.   The actual temperature rise and the reaction times are given in Tables X and XI.   The products were washed four times with deionized water.

Alkali Extraction

The chlorited product was extracted with 5% sodium hydroxide, based on the original ovendry material, at a pulp consistency of 10% for 60 minutes at 25°C. The product was washed three times with deionized water, then soaked in dilute acetic acid solution (3% acetic acid based on the original ovendry material) for two hours at room temperature, and then washed four times with deionized water.

CHLORINE DIOXIDE-ALKALI DELIGNIFICATION

All reactions were carried out in plastic bags with the products being mixed at regular intervals.   Pulp washings, when carried out, were done with deionized water except after the final hypochlorite bleach stage where distilled

water was used.   Dewatering was effected by a laundry-type spin drier using a nylon bag to contain the reacted products.

Alkali Conditioning

Where included, alkali conditioning was carried out under conditions recorded in the tables.   The collected products were washed four times with water.

First and Second Lignin Modifications

Lignin modifications were carried out using conditions as recorded in the tables.   At the end of each reaction time, the fibrous product was collected and dewatered in a spin drier, and washing was restricted to using only the water required to transfer the product into the nylon bag.

First and Second Alkali Extractions

Alkali extractions were carried out using conditions as recorded in the tables.   All extracted products were washed with water and those from the first extraction were passed to the second lignin modification.   Whether or not products from the second alkali extraction were soaked in acid is noted elsewhere in this report.

Hypochlorite Reaction

Reactions with buffered hypochlorite were carried out as noted in the tables.   The reacted products were washed with distilled water, soaked in dilute hydrochloric acid at a pH of 4 for 30 minutes, and then washed again with distilled water.

Screening and Centricleaning

Screening was carried out in a pulsating flat-bed screen with 0.006-in. slots. Distilled water was used with the accepts being collected on a muslin-covered washbox and the water draining from the box being recycled back to the screen.

Centricleaning was carried out at 0.5% consistency in distilled water, using a Bauer centricleaner model no. 600N fitted with a 1/8-in. tip and with the inlet pressure at 42 p.s.i.

PULP EVALUATION

Brightness handsheets were made from the unbeaten pulps according to TAPPI Standard T 218 os-69 but with the handsheets being formed from both 95% ethyl alcohol and distilled water.

The pulps were beaten in a 1-1/2 lb. Valley beater. Full details of the beating procedure, handsheet forming, and handsheet testing are given in Report Eight. The M.I.T. folding endurance values were corrected to a constant handsheet basis weight of 60.0 g. (o.d.)/m.^{2} by simple proportion. The Bendtsen smoothness tests were carried out on the rough side of the 1.0-g. handsheets, which had been used for the zero-span tensile tests, essentially according to the Bendtsen Handbook for the Model VI Smoothness and Porosity Tester, issued by Anderson and Sorensen (1964). Specific scattering coefficients and specific absorption coefficients (8, 9) were determined using a GE recording spectrophotometer, serial no. 716228, at a wavelength of 650 nm. with the "matte" side of the handsheet sample facing the incident light beam. The two values measured were reflectance, R_∞, and transmittance, T. Conditioned basis weights (73°F. and 50% R.H.), determined on 7/8-in. disks which were punched out from the area which had received the incident beam, were used in the calculations.

HYDRODYNAMIC EVALUATION

Drainage resistance and pulp compressibility were measured and the specific surface and specific volume data were calculated as described in Report Eight. However, for Pulp R, the drainage resistance was measured by a special research-model constant-rate filtration apparatus (10).

ACKNOWLEDGMENTS

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APPENDIX I

NOTES ON CODES

In this report, alphabetic codes have been used to identify various materials as summarized below.

A-G, H-J, and I-K with the prefix "Pulp" are for aspen chlorine dioxide-alkali pulps prepared as in Tables I, V, and VI, respectively, from S185 Bauer-fiberized chips.

L-R and S-X are for aspen and red maple OVP Asplund-fiberized chips, these materials being produced as in Tables X and XI, respectively.   Y is for red maple S185 Bauer-fiberized chips (see Table XIV).

Mc-Rc and Sc-Xc with the prefix "Pulp" are for aspen and red maple chlorite-alkali pulps, the complete evaluation data for which are in Appendix IV.

O, P, and R with the prefix "Pulp" are for chlorine dioxide-alkali pulps prepared as in Table XV from the correspondingly coded fiberized chips.

Su-Vu, Sb-Vb, and Yu and Yb with the prefix "Pulp" are for red maple chlorine dioxide-alkali pulps prepared as in Table XIII from the correspondingly coded fiberized chips.

APC and MPC are for chlorite-alkali pulps made from aspen and red maple pin chips, respectively.   (See Tables XXI and XXII in Appendix IV.)

APPENDIX II

TABLE XX

HANDSHEET DATA FOR WATER CHLORINE DIOXIDE-ASPEN PULPS H, I, J, AND K

	Pulp H[a]					Pulp I[a]				Pulp J[a]					Pulp K[a]			
	0	4[b]	8[b]	16[c]	22[b]	0[d]	5[c]	25[c]	50[c]	0	3[b]	8[b]	12[b]	15[b]	5[c]	15[c]	25[c]	35[c]
Beating time, min.[b] or sec.[c]	0	4.0	8.1	17.9	22.0	4.6	9.4	11.6	19.2	—	4.8	7.8	15.1	27.1	3.2	11.0	13.7	17.3
Canadian drainage time, sec.	410	330	295	185	125	290	225	160	115	350	325	235	160	130	350	210	175	150
Density, g./cc.	0.626	0.677	0.720	0.765	0.808	0.727	0.768	0.802	0.813	0.651	0.666	0.725	0.752	0.784	0.705	0.735	0.754	0.795
Opacity, %	79	78	76	72	66	69	66	58	57	77	76	74	71	68	67	64	61	56
Breaking length, km.	7.3	6.2	5.3	10.1	10.9	7.0	10.1	11.1	11.0	7.2	5.5	3.0	3.8	10.2	9.2	10.1	10.5	10.3
Stretch, %	2.1	2.2	2.5	2.4	2.5	2.6	2.8	2.9	3.0	2.1	2.3	2.3	2.4	2.4	2.6	2.5	2.5	2.5
Tensile energy absorption, g.cm./cm.²	65	75	96	105	114	80	120	137	140	65	73	39	97	103	104	108	118	112
Tensile stiffness, kg./cm.	515	547	584	618	655	516	564	648	612	499	557	555	595	614	564	600	597	537
Burst factor	36	43	50	48	61	48	48	65	60	37	44	51	55	59	51	54	61	60
... (Elmendorf)	61	62	61	55	52	63	58	54	52	56	60	56	56	54	51	59	61	60
In-plane tear, g.cm./cm.	55	56	58	58	54	—	54	56	54	50	46	49	48	45	60	61	61	61
Zero-span breaking length, km.	16.0	17.4	16.5	15.6	15.4	16.2	19.3	18.5	12.8	15.4	17.6	18.5	18.2	18.7	16.3	18.1	18.0	17.1
M.I.T. fold	55	56	157	569	750	37	123	1050	925	74	130	310	499	830	170	597	692	1200
Specific scattering coefficient, 650 m...	268	255	227	193	171	246	222	157	150	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

a. Semibleached materials, representing 80% of flat screen accepts for Pulps H, I, and J; 84% for Pulp K.
b. Minutes in Valley beater with 2.0-kg. bedplate load.
c. Seconds at 25% s.c. with 3.4-kg./cm. beating pressure, PFI mill.
d. Disintegrated for 600 rev. counts in British disintegrator.
e. n.d. = not determined.

APPENDIX III

CANADIAN FREENESS VERSUS pH AND PULP HISTORY

When the screen accepts from Pulp J were soaked in acid as was Pulp A and freeness on the washed pulp determined at different pH values by appropriate addition of alkali or acid, the data obtained may be represented by Curve I in Fig. 37. When the acid-soaked screen accepts of Pulp J were extracted with hot alkali (final pH 11.4) and freeness on the washed pulp determined at different pH values, the data obtained may be represented by Curve II in Fig. 37. Curve III was obtained similarly to Curve II except that centricleaner rejects from Pulp K were used. Since it is known that freeness can be influenced by changes in pH, a laboratory-prepared aspen unbleached kraft pulp was used to obtain the curves for a kraft pulp in Fig. 37.
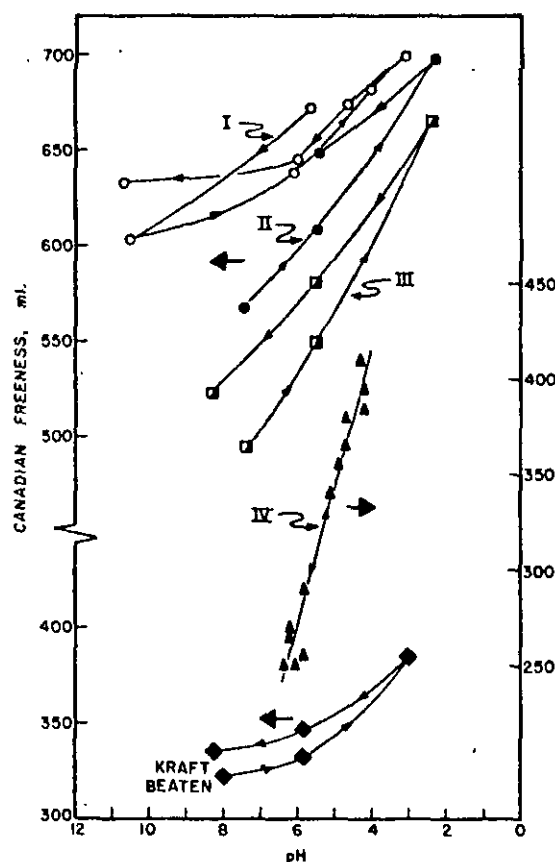
Figure 37. Aspen Chlorine Dioxide-Alkali Pulps and an Aspen Kraft Pulp — Canadian Freeness vs. pH

Subsequently, centricleaner accepts from Pulp J were extracted with hot

alkali (final pH 11.1) and freeness of the distilled-water-washed pulp determined

at different pH values using the same approach as for Curves II and III.   Results

were obtained as for Curve IV.   In this instance, there appears to be a simpler

relationship of freeness vs. pH.   This is believed to be associated with more

meticulous washing and/or more time being allowed for the suspended pulps to reach

equilibrium conditions and/or there being no need to apply any corrections for

temperature differences.

Since the history of a pulp can influence freeness, the practice of

leaving pulps in dilute acid after alkali extraction has been continued for a time

to ensure a common basis of treatment for comparing handsheet properties.

APPENDIX IV

TABLE XLV

HANDSHEET DATA FOR ASPEN CHLORITE-ALKALI PULPS

Beating time, min.[a]	Pulp M[?]					Pulp Mc								Pulp Oc						Pulp Pc				
	0	1	2	3	5	0	1	2	4	7	0	1	2	3	5	0	1	2	4	7					
Canadian freeness, ml.	320	280	280	240	215	400	350	325	265	225	235	210	190	175	145	105	230	305	270	310					
Handsheet drainage time, sec.	7	7	8	9	11	6	7	7	8	11	8	9	10	9	12	n.d.	n.d.	n.d.	n.d.	n.d.					
Handsheet density, g./cc.	0.725	0.729	0.733	0.750	0.769	0.725	0.735	0.735	0.744	0.774	0.740	0.747	0.764	0.767	0.776	0.716	0.726	0.725	0.735	0.751					
Scott internal scattering coefficient[b]																									

TABLE XXII

HANDSHEET DATA FOR RED MAPLE CHLORITE-ALKALI PULPS

	Pulp Sc					Pulp Tc					Pulp Uc					Pulp Vc				
Beating time, min.[a]	1	5	6	10	15	1	2	4	6	8	1	3	6	15	25	1	3	6	9	11
Canadian freeness, ml.	550	500	440	365	260	215	190	155	140	125	575	555	490	350	200	210	180	145	115	100
Handsheet drainage time, sec.	4.5	4.8	5.2	7.5	15.6	6.0	7.0	7.8	9.6	13.0	4.7	4.6	4.8	7.3	41	5.5	6.0	7.4	10.0	14.6
Density, g./cc.	0.615	0.651	0.676	0.715	0.755	0.742	0.757	0.755	0.781	0.788	0.641	0.653	0.676	0.738	0.804	0.697	0.716	0.719	0.749	0.763
Bendtsen smoothness, ml./min., back side	2650	2140	1770	1400	1320	526	550	529	596	575	1390	1040	936	785	805	416	499	465	524	548
Sp. scattering coeff., 650 nm.	199	202	210	192	160	248	258	238	218	207	247	251	245	202	150	277	260	255	251	215
Breaking length, km.	5.64	6.65	7.81	9.14	10.0	9.07	9.21	9.36	9.84	9.86	6.33	6.58	7.51	9.55	10.5	8.01	8.29	8.56	8.95	9.15
Stretch, %	1.6	2.0	2.4	2.8	2.9	2.9	2.9	2.9	3.0	3.0	2.0	2.0	2.4	3.0	3.1	2.5	2.7	2.9	2.8	2.9
Tensile energy absorption, g. cm./cm.[2]	36.1	54.8	80.4	109	124	112	113	115	125	124	52.5	55.2	75.1	124	140	84.4	99.1	106	115	119
Tensile stiffness, kg./cm.	483	504	553	567	589	565	563	579	607	599	486	490	535	569	601	569	549	554	589	576
Burst factor	26.0	33.1	41.7	53.1	60.5	52.7	56.5	56.6	60.5	61.0	33.2	36.0	41.9	58.2	67.4	45.0	51.5	53.5	59.4	65.4
Tear factor × yield/65	56.6	57.0	55.4	54.8	56.4	61.7	57.8	58.6	56.7	55.1	64.5	61.7	63.6	62.6	54.9	63.2	64.8	63.7	60.9	64.0
In-plane tear, g. cm./cm.	46.5	49.0	52.1	53.0	53.8	57.4	59.2	60.2	59.3	59.8	48.8	48.5	53.7	57.9	58.2	52.0	55.9	58.5	59.6	60.7
Zero-span b.l. × yield/65, km.	14.2	14.8	15.7	16.4	17.1	17.1	16.9	17.6	17.5	17.4	15.8	15.8	16.8	17.7	17.9	16.6	17.0	16.2	15.5	16.9
M.I.T. fold	19	74	180	448	951	147	146	215	242	201	33	49	90	508	1460	79	103	147	226	310

	Pulp Wc					Pulp Xc					Pulp MPC[b]				Pulp Vc[c]				
Beating time, min.[a]	1	3	6	15	26	0	2	4	6	10	1	3	7	15	1	3	5	9	11
Canadian freeness, ml.	520	500	465	335	190	350	300	265	235	185	635	615	575	460	260	230	210	150	115
Handsheet drainage time, sec.	4.8	4.9	5.6	8.5	42.5	4.9	5.1	5.6	6.1	8.1	4.5	4.5	8.8	115	5.5	5.9	6.8	8.0	10.7
Density, g./cc.	0.658	0.671	0.696	0.752	0.813	0.682	0.698	0.701	0.708	0.724	0.691	0.708	0.724	0.729	0.705	0.714	0.725	0.749	0.762
Bendtsen smoothness, ml./min., back side	813	790	773	5??	659	468	444	514	465	501	512	535	616	702	n.d.[d]				
Sp. scattering coefficient, 650 nm.	275	270	256	212	151	295	289	296	278	258	278	261	243	220	267	256	248	230	218
Breaking length, km.	6.80	7.21	7.80	9.62	10.7	7.26	7.73	7.97	8.25	9.06	7.66	8.00	9.10	9.80	8.02	8.27	8.65	9.2?	9.45
Stretch, %	2.2	2.3	2.6	3.2	3.3	2.4	2.4	2.5	2.6	2.9	1.4	1.4	1.6	1.6	2.6	2.7	2.8	3.0	3.0
Tensile energy absorption, g. cm./cm.[2]	64.1	72.7	86.5	152	155	73.0	77.5	81.8	92.0	112	43.9	45.4	58.4	63.1	61.8	95.5	106	118	122
Tensile stiffness, kg./cm.	446	510	521	574	617	479	516	527	517	555	577	610	624	648	541	548	570	582	581
Burst factor	38.5	40.2	46.8	61.1	70.4	39.6	44.2	46.1	47.3	53.6	35.6	39.5	42.3	44.7	48.7	49.6	54.6	57.0	60.5
Tear factor × yield/65	61.1	62.7	59.9	59.9	52.9	53.4	52.1	54.7	60.9	58.7	62.5	60.3	58.6	65.4	63.6	63.4	64.3	64.5	64.2
In-plane tear, g. cm./cm.	47.4	53.3	54.3	59.5	60.1	49.9	52.2	49.8	51.2	56.6	43.3	43.9	45.5	46.6	56.9	57.8	57.7	60.9	62.8
Zero-span b.l. × yield/65	16.8	16.2	17.6	17.4	17.4	15.1	15.4	15.5	15.5	15.6	24.6	25.5	23.9	22.4	16.2	16.6	16.6	17.0	16.7
M.I.T. fold	12	47	95	446	1480	44	57	66	76	83	35	48	56	84	75	81	82	170	205

[a] Valley beater, 3 G-mm. bedplate load

[b] Chlorite-alkali pulp from pin chips.

[c] Repeat delignification and evaluation.

[d] n.d. = not determined

APPENDIX V

PRELIMINARY CHLORINE DIOXIDE-ALKALI DELIGNIFICATION OF RED MAPLE

For preliminary experiments on delignification of red maple, the V-coded fiberized material (Table XI) was used. The initial conditions tried for delignification were:

(a) similar to those for Pulp H (Table V), and

(b) similar to (a) but preceded by alkali conditioning as in Table XXIII. Both pulps were relatively hard to separate into fibers, and after PFI milling, the pulp prepared without alkali conditioning had 6.0% screen rejects, or twice the amount with an alkali conditioning step.

TABLE XXIII

PRELIMINARY CHLORINE DIOXIDE-ALKALI PULPING OF FIBERIZED RED MAPLE (CODE V — TABLE XI)

Run	ClO_2, %[a]	NaOH, %	Cl_2, %	Time, min.	Final pH	Yield, %	Rejects, % o.d.p.	Klason + Acid-sol. Lignin, %	Canadian Freeness	Brightness, TAPPI
Alkali conditioning — consistency 6.0%; temp. 60°C.										
i						nil				
ii	-	1.0	-	10	9.5	-	-	-		
Lignin modification — consistency 6.0%; temp. 25–35°C.										
i	4.97	-	0.88	55	1.9	-	-	-		
ii	4.97	-	0.88	60	1.9	-	-	-		
Alkali extraction — consistency 10%; temp. 70°C.										
i	-	6.0	-	20	9.1	-	-	-		
ii	-	5.5	-	20	9.2	-	-	-		
Lignin modification — consistency 10%; temp. 25–35°C.										
i	2.53	-	0.45	75	2.5	-	-	-		
ii	2.53	-	0.45	75	2.5	-	-	-		
Alkali extraction — consistency 15%; temp. 70°C.										
i	-	2.6	-	20	9.6	74	6.2[b]	8.1 + 3.7	730[c]	49
ii	-	2.5	-	20	8.7	75	3.0	8.8 + 4.0	705[c]	54
Hypochlorite reaction[d] — consistency 20%; temp. 40°C.										
i	-	0.75	3.0	25	8.1	-	-	-	680[c]	76
i	-	0.90	4.5	60	8.3	-	-	-	665[c]	81
ii	-	0.75	3.0	45	7.9	-	-	-	650[c]	78
ii	-	0.90	4.5	52	8.1	-	-	-	610[c]	81

[a] All percentages on an o.d. fiberized chip basis. Fiberized chip Klason lignin, 23.7%; acid-soluble lignin, 4.6%.

[b] Dilute acid soak after alkali extraction, followed by 15 sec. at 25% o.d.p. consistency in PFI mill with 3.4-kg./cm. load before screening.

[c] After 600 rev. counts in a British disintegrator; pH ≈ 6.

[d] Screen accepts used for reaction with hypochlorite.

APPENDIX VI

TABLE XXIV

HANDSHEET DATA FOR RED MAPLE CHLORINE DIOXIDE-ALKALI PULPS PREPARED AS IN TABLE XIII

Pulp code	Vu						Yu					Uu				
Beating time, min.[a]	1	3	6	10	16	22	1	2	3	7	10	0	1	2	5	9
Canadian freeness, ml.	590	570	480	590	225	135	450	380	550	220	150	410	360	335	250	140
Handsheet drainage, sec.	4.7	4.6	4.8	5.0	6.0	12.0	5.1	5.6	5.8	8.9	16.8	4.8	4.9	5.2	6.2	11.2
Density, g./cc.	0.564	0.579	0.602	0.622	0.665	0.709	0.627	0.635	0.639	0.683	0.723	0.599	0.616	0.623	0.653	0.688
Bendtsen smoothness, ml./min.[b]	1880	n.d.[c]	1260	n.d.	1140	n.d.	1930	2090	1900	1600	1100	1770	n.d.	1610	n.d.	1410
Sp. scattering coeff., 650 nm.	n.d.	267	n.d.	259	n.d.	209	223	223	223	207	178	255	n.d.	253	n.d.	210
Breaking length, km.	4.6	5.3	5.9	6.1	7.4	8.4	6.5	6.8	7.0	8.2	8.9	6.2	6.7	6.8	7.5	8.4
Stretch, %	1.6	1.7	1.9	2.0	2.3	2.6	2.4	2.5	2.5	2.8	2.9	2.0	2.3	2.3	2.5	2.6
T. E. A., g. cm./cm.[2]	31	38	47	52	73	97	-	73	75	99	108	54	n.d.	69	n.d.	98
Tensile stiffness, kg./cm.	388	413	440	442	495	526	455	456	477	517	551	488	n.d.	478	n.d.	540
Burst factor	21	24	28	32	41	47	35	37	39	45	51	35	n.d.	39	n.d.	51
Tear factor x yield/65	65	66	63	63	65	62	61	60	60	55	54	68	65	64	63	64
In-plane tear, g. cm./cm.	38	40	41	42	47	50	51	50	49	50	51	n.d.	48	n.d.	47	n.d.
Zero-span b.l. x yield/65, km.	14.5	16.4	16.3	17.1	17.4	18.0	12.5	12.7	13.9	14.6	14.4	15.5	16.1	16.0	16.2	17.7
M.I.T. fold	10	17	21	54	79	220	78	81	89	205	328	49	78	70	127	320

Pulp code	Vb						Yb					Ub				
Beating time, min.[a]	1	3	6	10	15	22	0	1	2	4	6	0	1	2	3	5
Canadian freeness, ml.	520	480	440	360	265	150	370	330	285	230	175	355	305	265	220	175
Handsheet drainage, sec.	4.7	4.9	4.8	5.3	6.4	11.5	5.5	6.0	6.6	8.2	12.1	5.0	5.1	6.0	6.3	8.1
Density, g./cc.	0.594	0.614	0.644	0.656	0.690	0.739	0.675	0.685	0.715	0.734	0.750	0.673	0.684	0.681	0.696	0.710
Bendtsen smoothness, ml./min.[b]	1650	1510	1080	900	960	898	1410	1310	1470	1520	1320	1190	1490	1150	1290	858
Sp. scattering coeff., 650 nm.	n.d.	277	n.d.	265	n.d.	210	209	201	184	173	173	228	n.d.	228	n.d.	215
Breaking length, km.	5.5	5.9	6.6	7.1	8.0	9.0	7.6	8.0	8.5	9.1	9.3	7.8	8.0	8.0	8.4	8.8
Stretch, %	1.9	2.0	2.4	2.6	2.8	2.9	2.9	3.1	3.1	3.3	3.2	2.6	2.9	2.7	2.9	2.9
T. E. A., g. cm./cm.[2]	46	50	69	80	100	118	90	101	107	123	123	89	n.d.	97	n.d.	113
Tensile stiffness, kg./cm.	444	456	485	495	529	570	379	381	399	409	420	504	n.d.	550	n.d.	579
Burst factor	26	30	34	38	45	55	47	49	53	58	60	45	n.d.	50	n.d.	56
Tear factor x yield/65	65	61	60	62	65	60	60	57	55	53	53	63	63	62	64	60
In-plane tear, g. cm./cm.	42	46	47	50	52	55	51	52	53	54	50	n.d.	50	n.d.	50	n.d.
Zero-span b.l. x yield/65, km.	15.5	15.7	16.8	16.7	17.2	17.1	14.0	15.5	16.4	16.6	16.8	15.6	16.2	16.4	16.5	17.7
M.I.T. fold	15	19	30	39	111	269	236	260	544	604	521	128	181	154	252	277

[a] Valley beater with 2.0-kg. bedplate load.

[b] Back side of handsheet.

[c] n.d. = not determined.

TABLE XXV

HANDSHEET DATA FOR RED MAPLE CHLORINE DIOXIDE-ALKALI PULPS FROM FIBERIZED MATERIALS S AND T

Pulp code	Su					Tu					Tb				
Beating time, min.[a]	0	1	2	4	6	0	1	3	5	7	0	1	2	3	4
Canadian freeness, ml.	360	320	285	215	165	360	340	260	195	145	280	235	205	185	160
Handsheet drainage time, sec.	5.3	5.7	6.1	6.7	10.7	5.5	6.0	6.9	9.6	14.6	6.1	7.2	8.0	10.1	12.6
Density, g./cc.	0.585	0.595	0.609	0.637	0.687	0.585	0.599	0.623	0.641	0.668	0.665	0.677	0.679	0.692	0.718
Bendtsen smoothness, ml./min.[b]	2700	n.d.[c]	2840	n.d.	2200	2650	n.d.	1960	n.d.	2040	1730	1890	1950	2150	1570
Specific scattering coeff., 650 mm.	221	n.d.	225	n.d.	188	207	n.d.	212	n.d.	179	199	n.d.	197	n.d.	175
Breaking length, km.	6.7	7.1	7.2	8.1	8.8	6.7	7.0	7.7	8.1	8.6	8.3	8.8	8.8	9.0	9.4
Stretch, %	2.1	2.1	2.1	2.4	2.5	2.1	2.2	2.5	2.6	2.6	2.6	2.8	2.8	2.7	2.7
Tensile energy absorption, g. cm./cm.^{2}	59	64	62	81	90	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tensile stiffness, kg.-/cm.	465	469	478	486	549	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Burst factor	33	36	39	42	51	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tear factor x yield/65	65	64	57	58	56	62	63	60	59	57	57	56	56	57	58
In-plane tear, g. cm./cm.	52	50	52	53	56	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Zero-span b.l. x yield/65, km.	14.0	14.3	15.2	16.2	17.2	14.3	15.4	15.5	16.7	17.2	15.8	16.9	16.3	16.5	17.4
M.I.T. fold	99	117	144	194	381	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

[a] Valley beater with 2.0-kg. bedplate load.

[b] Back side of handsheet.

[c] n.d. = not determined.

APPENDIX VII

TABLE XVI

HANDSHEET DATA FOR ASPEN CHLORINE DIOXIDE-ALKALI PULPS PREPARED AS IN TABLE XV

Pulp code	D				C					P				
Beating time, min [a]	0	2	5	7	0	2	5	12	24	0	2	8	16	24
Canadian freeness, ml	400	350	275	100	530	480	430	315	190	610	560	400	320	165
Handsheet drainage time, sec	nd	nd	nd	nd	44	46	52	6.3	12.1	42	47	51	62	13.5
Density, g/cc	0.687	0.716	0.749	0.784	0.624	0.649	0.674	0.716	0.703	0.610	0.654	0.677	0.722	0.758
Gurley smoothness, ml/min [b]	1870	1170	890	810	1420	1400	850	760	1000	1900	1720	880	750	330
Specific scattering coefficient, cm²/g	235	235	217	-	257	259	244	222	138	246	249	243	211	181
Breaking length, km	8.6	9.4	10.0	10.8	6.8	7.4	8.2	3.5	3.5	6.1	6.9	7.9	9.2	9.7
Stretch, %	2.6	2.7	2.6	2.7	1.9	2.1	2.2	2.5	2.5	1.8	2.1	2.3	2.5	2.4
Tensile energy absorption, g·cm/cm²	93	103	107	117	56	67	76	93	111	46	63	75	96	98
Tensile stiffness, kg/cm.	526	551	587	615	481	485	520	557	606	473	507	538	611	511
Burst factor	48	54	53	53	36	39	47	57	63	31	36	44	55	60
Tear factor x field/65	59	55	54	54	64	64	59	59	54	65	67	59	59	52
In-plane tear, b cm/cm	48	47	47	44	48	49	50	51	49	47	45	50	48	46
Zero-span breaking length x field/65, c	16.6	17.7	10.6	19.9	14.7	15.7	16.4	16.7	17.4	14.6	14.8	16.4	17.5	17.2
M I T fold	256	330	636	1205	33	64	108	232	690	21	26	64	182	387

[a] Valley beater with 2.0-kg bedplate load

[b] Back side of handsheet

APPENDIX VIII

EVALUATION OF PULP R.

HANDSHEET DATA

Of the materials available for evaluation after other studies, Pulp R was distinguished by being derived from chips that had been fiberized above the point of plasticization, as judged on the basis discussed in connection with Fig. 14-16 and Tables X-XI.   Handsheet data for Pulp R are given in Table XXVII.

TABLE XXVII

ASPEN — HANDSHEET DATA FOR CHLORINE DIOXIDE-ALKALI PULP R

Pulp code	R				
Beating time, min.[a]	0	2	9	14	18
Canadian freeness, ml.	570	500	350	235	155
Handsheet drainage, sec.	4.7	4.8	6.0	10.6	22.8
Density, g./cc.	0.642	0.669	0.717	0.758	0.801
Bendtsen smoothness, ml./min.[b]	1450	1120	688	711	737
Specific scattering coefficient[c]	250	245	215	186	151
Breaking length, km.	7.15	7.93	9.54	10.2	10.5
Stretch, %	2.0	2.3	2.6	2.6	2.5
Tear factor	60.7	59.9	56.3	52.8	49.3
Tear factor x yield/65	63	62	58	55	51
Zero-span breaking length, km.	14.3	15.0	16.2	16.0	15.9
Zero-span b. l. x yield/65	14.8	15.5	16.8	16.6	16.5
M.I.T. fold	65	79	318	778	1135

[a] Valley beater, 2.0-kg. weight.   [c] 650 nm.

[b] Rough side of handsheet.

.This pulp beat more rapidly and gave higher density handsheets than either of Pulps O·or P, but it has significantly different properties from Pulp D. For example, handsheet density was 0.717 g./cc. for Pulp R after 9 min. beating, whereas that density was reached in only 2 min. for Pulp D.

When comparing Pulp R with Pulps O and P, it is desirable to note that the time at fiberization temperature of the former was between that for Pulps O and P, but the fiberization temperature was higher, namely 165 instead of 158°C. The higher temperature could have resulted in more chemical changes during fiberization. However, about the only positive indication of this is some loss in zero-span breaking length.

HYDRODYNAMIC PROPERTIES· OF PULP R

The hydrodynamic properties determined for Pulp R are given in Table XXVIII.

TABLE XXVIII

HYDRODYNAMIC PROPERTIES OF ASPEN CHLORINE DIOXIDE-ALKALI PULP R.

Beating time, min.	9	18
Canadian freeness, ml.	350	155

ΔP, cm. H_2O	$R \times 10^{-8}$, cm./g.	
10	1.70	4.69
20	2.53	7.51
30	3.27	10.1
40	3.96	12.6
50	4.62	15.0
60	5.26	17.3
70	5.90	19.6
80	6.50	21.8
90	7.11	24.0

M, c.g.s. units	0.001185	0.00122
N	0.144	0.144
$\langle S_w \rangle$, cm.^{2}/g.	3.49	3.59
$\langle v \rangle$, cc./g.	3.49	3.59

APPENDIX IX

TABLE XXIX

PREPARATION OF ASPEN KRAFT PULP FOR REFERENCE

Liquor/wood	4.0	Max. temp., $^{\circ}$C.	174
Active alkali, % NaOH	19.4	Time to max. temp., min.	90
Sulfidity, %	30.0	Time at max. temp., min.	75
Unscreened yield, %	51.6	Blowdown to 80 p.s.i., min.	5
Rejects, %	0.5	Kappa number	12.2

HANDSHEET DATA (VALLEY BEATER)

Beating time, min.[a]	0	12	24	28
Canadian freeness, ml.	610	435	280	190
Density, g./cc.	0.593	0.711	0.773	0.797
Breaking length, km.	4.65	8.88	10.8	11.3
Stretch, %	1.4	2.4	2.7	2.8
Tensile energy absorp., g.cm./cm.^{2}	28.2	88.8	123	134
Tensile stiffness, kg./cm.	454	561	665	671
Burst factor	20.9	49.2	63.1	65.1
Tear factor (Elmendorf)	69.5	78.8	69.6	64.7
Tear factor x yield/65	54.6	62.0	54.7	50.9
In-plane tear, g.cm./cm.	40.4	60.1	62.0	61.8
Zero-span breaking length, km.	17.7	20.5	20.3	20.4
Zero-span breaking length x yield/65	13.9	16.1	16.0	16.0
M.I.T. fold	7	135	882	1429
z-direction tensile, kg./cm.^{2}	5.4	13.7	20.8	22.7
Spec. scattering coeff. (650 nm.)	382	287	229	219
Bendtsen smoothness, ml./min.[b]	588	471	497	502

[a] 5.5-kg. weight on end of bedplate lever.

[b] Rough side of handsheet.

TABLE XXX

PREPARATION OF MAPLE KRAFT PULP FOR REFERENCE

Liquor/wood	4.0	Max. temp., °C.	180
Active alkali, % Na$_2$O	15	Time to max. temp., min.	90
Sulfidity, %	28	Time at max. temp., min.	60
Unscreened yield, %	50.3	Blowdown to 80 p.s.i., min.	15
Screen rejects, %	1.6	Kappa number	14.4

HANDSHEET DATA (VALLEY BEATER)

Beating time, min.[a]	1	3	6	10	16	24
Canadian freeness, ml.	525	520	465	420	340	195
Handsheet drainage time, sec.	4.8	4.9	4.8	5.4	7.0	12.3
Density, g./sec.	0.608	0.645	0.667	0.701	0.757	0.819
Breaking length, km.	5.97	6.93	7.93	8.93	10.4	11.3
Stretch, %	1.1	1.3	1.6	2.0	2.5	2.9
Tensile energy absorp., g.cm./cm.^{2}	25.8	36.1	52.5	73.4	106	136
Tensile stiffness, kg./cm.	565	578	598	615	648	671
Burst factor	22.3	28.7	35.7	44.0	58.1	70.5
Tear factor (Elmendorf)	50.6	58.7	69.9	73.9	73.7	63.8
Tear factor x yield/65	37.9	44.0	52.4	55.4	55.2	47.8
In-plane tear, g.cm./cm.	25.1	39.2	45.2	50.9	59.6	59.2
Zero-span breaking length, km.	23.8	23.5	22.5	22.4	21.9	21.6
Zero-span b. l. x yield/65, km.	17.8	17.6	16.9	16.8	16.4	16.2
M.I.T..fold	7	13	30	84	612	2250
Spec. scattering coeff. (650 nm.)	418	399	368	336	280	212
Bendtsen smoothness, ml./min.[b]	367	520	302	298	300	355

[a] Bedplate weight 5.5 kg.

[b] Rough side of handsheet.

APPENDIX X

TABLE XXXI

BLEACHED BAGASSE HANDSHEET DATA

Beating time, min.[a]	0	3	5	7	9	12
Canadian freeness, ml.	490	410	365	300	235	150
Handsheet drainage time, sec.	5.3	6.0	6.8	8.4	10.8	19.5
Handsheet density, g./cc.	0.651	0.689	0.696	0.722	0.729	0.758
Spec. scattering coeff., 650 nm.	273	257	249	232	226	196
Spec. absorption coeff., 650 nm.	4.24	4.37	3.97	4.77	5.11	6.13
Breaking length, km.	5.44	6.27	6.53	7.06	7.20	7.55
Stretch, %	2.8	2.7	2.6	2.7	2.5	2.5
Tensile energy absorp., g.cm./cm.^{2}	68.8	75.2	76.6	85.4	80.7	83.4
Tensile stiffness, kg./cm.	385	435	463	472	504	514
Burst factor	33.0	39.0	39.5	42.1	42.9	46.6
Tear factor	60.4	56.2	54.5	51.9	49.2	48.9
In-plane tear, g.cm./cm.	51.4	46.6	45.1	43.5	42.4	41.5
Zero-span breaking length, km.	11.2	11.2	11.4	12.1	12.1	12.6
M.I.T. fold	39	71	109	165	230	332
Bendtsen smoothness (back), ml./min.	851	851	824	828	868	924
TAPPI brightness (water), %	84.5					
TAPPI brightness (EtOH), %	85.5					

[a] Valley beater with 5.5-kg. bedplate load.

APPENDIX XI

ALKALINE t-BUTYL HYDROPEROXIDE (TBHP) AS A SELECTIVE DELIGNIFYING AGENT

Alkaline t-butyl hydroperoxide (TBHP) has been used in an exploratory 4-stage (alkaline TBHP, NaOH extraction, alkaline TBHP, NaOH extraction) delignification of a sample of red maple fiberized chips. In order to obtain a better idea of the role of TBHP during delignification, a parallel delignification was carried out with only the equivalent free NaOH present in the four stages.

A summary of the experimental data is given in Table XXXII.

It can be seen that the final yield obtained when using a total of 10% TBHP based on the original ovendry fiberized material was 82.5%. This is well above the yields obtained using similar percentages of chlorine dioxide. In particular, this alkaline-TBHP pulp should be compared with Pulps Vu and Vb prepared from the same lot of fiberized red maple chips. A tabulated comparison is made in Table XXXIII.

The final yield obtained with the four stages of sodium hydroxide was 86.6% and, as expected, the brightness of this bleached pulp was rather low (38.5).

Since t-butyl hydroperoxide does not appear to be promising as a selective delignifying agent, further experiments do not appear justified as a part of this project at present.

TABLE XXXII

DELIGNIFICATION OF FIBERIZED RED MAPLE CHIPS USING (1) ALKALINE t-BUTYL HYDROPEROXIDE AND (2) ALKALI ALONE

	TBHP-NaOH	NaOH		TBHP-NaOH	NaOH
Starting material	V	V			
Charge, as g. oven dry	20	50			
Stage 1			**Stage 4**		
TBHP, %[a]	5.0[b]	--	NaOH, %	2.7	2.7
NaOH, %	6.7	4.5	Consistency, %	10	10
Consistency, %	20	20	Temp., °C.	70	70
Temp., °C.	95	95	Time, min.	20	20
Time, min.	20	20	Final pH	12.5	12.3
Final pH	11.4	9.9	Wash	yes	yes
Wash	no	no			
			Yield, %	82.5	86.6
Stage 2			Klason lignin, %	15.9	18.8
NaOH, %	2.7	2.7	Acid-sol. lig., %	3.7	3.7
Consistency, %	10	10			
Temp., °C.	70	70	**Stage 5**		
Time, min.	20	20	Hypo. as Cl_2, %	5.4	5.6
Final pH	11.7	11.2	NaOH, %	0.2	0.2
Wash	yes[c]	yes	Consistency, %	10	10
			Temp., °C.	40	40
Stage 3			Time to exhaust, min.	35	15
TBHP, %	5.0[b]	--	Final pH	8.6	8.9
NaOH, %	6.7	4.5	Wash	yes	yes
Consistency, %	20	20			
Temp., °C.	95	95	Yield, %	82.5	86.6
Time, min.	20	20	G.E.	55.2	58.5
Final pH	12.2	11.8			
Wash	no	no			

[a] All percentages are on an o.d. fiberized chip basis.

[b] Residual TBHP — nil.

[c] Yield at this point — 87.1%.

TABLE XXXIII

COMPARISON OF ALKALINE TBHP AND CHLORINE DIOXIDE-ALKALI PULPS

Pulp	TBHP-NaOH	V	Vb
Total TBHP, %	10.0	--	--
Total ClO_2, %	--	7.5	7.5
Total Cl_2, %	--	1.3	1.3
Hypo. as Cl_2, %	5.4	--	3.0
Yield, %	82.5	69.5	65.7
Klason lignin, %	15.9[a]	4.5	2.0
Acid-soluble lignin, %	3.7[a]	4.3	0.9
G.E. brightness	55.2	--	80.8

[a] Data for unbleached pulp.