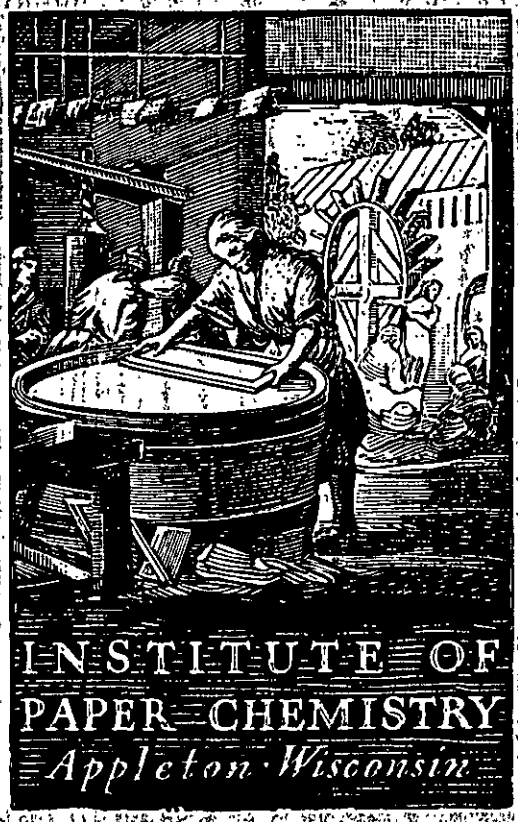

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SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS:

WATER BALANCE AND RELATED EXPERIMENTS, HIGH-CONSISTENCY GAS-PHASE OXIDATION, AND CHLORINE DIOXIDE-ALKALI PULPING WITH LESS OXIDANT

Research Grant

Project 2500

Report Fourteen

A Progress Report

to

THE GRANTORS

September 23, 1971

CONFIDENTIAL

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS: WATER BALANCE AND RELATED EXPERIMENTS, HIGH-CONSISTENCY GAS-PHASE OXIDATION, AND CHLORINE DIOXIDE-ALKALI PULPING WITH LESS OXIDANT

SUMMARY

Consideration has been given to water balance in a holopulping process. Related experiments have included dewatering to high consistency in a laboratory screw press and recycling of chlorine dioxide spent liquor. The influence on pulp properties of screw press dewatering was positive and somewhat analogous to high-consistency refining. There was no increase in chlorine dioxide consumption on recycling spent liquor from an aqueous-phase chlorine dioxide oxidation. It has been concluded that although the spent liquor stream from a complete holopulping process could be more dilute than from an existing chemical pulp mill, total liquor output is not seen now as a possible roadblock. Furthermore, it is anticipated that spent liquor output to a recovery system for producing a bleached hardwood pulp could be appreciably less than from a chemical pulp mill plus bleach plant.

Attention has been focused on high-consistency gas-phase reaction of fiberized chips using a stream of chlorine dioxide/steam. Experiments to date provide a firmer basis to foresee fiberized material being fed to a fluffer and reacting with a stream of chlorine dioxide/steam in a relatively short time. This opens the way for the possible direct use of chlorine dioxide generator gas and the lowering of costs. Consideration has been given to the kind of reactor that might conceivably be used for high-consistency gas-phase oxidation of fiberized chips.

Investigations on chlorine dioxide-alkali pulping with less oxidant have demonstrated that bleached hardwood holopulps can be obtained using as little as

6% chlorine dioxide all in one stage. What this means in terms of reduced need to generate chlorine dioxide for a pulp mill is discussed. Substantial savings in chemical and capital costs, as previously estimated, follow from this significant reduction in the amount of chlorine dioxide used.

WATER BALANCE AND RELATED EXPERIMENTS

INTRODUCTION

The importance of taking water balance into account in overall consideration of a holopulping process was stressed in Progress Report Eleven (1). In a general sense, there is some analogy between the situation that could be encountered in a holopulping system and the situation that currently exists in relation to disposing of bleach plant effluents. Minimizing the total volume of effluent is an important objective in both cases. Thus, practical progress in reducing the volume of bleach plant effluent is of potential interest when considering a holopulping process.

From panel discussions at the 1970 TAPPI Bleaching Conference, it was apparent that water usage certainly could be reduced to 10,000 gal./ton pulp. At least one report (2) showed water usage, excluding water to transport pulp, could be reduced to about 6400 gal./ton pulp. Continuing activity in this area by members of the TAPPI panel has shown water usage can be lowered considerably below the above figure. Bleach plant effluent flows of under 5000 gal., or say 42,000 lb. per ton pulp, can be foreseen. This level of flow is envisaged as being achieved in a plant with countercurrent drum washing with reduced water input on the washers and with water recycle in the chlorination stage or its equivalent.

It is interesting to compare this envisaged flow of bleach plant effluent with the flow of spent liquor to a recovery system in a conventional pulp mill. There is some variation in the amount of spent liquor that reflects differences in pulp mill operating conditions such as liquor-to-wood ratio, the amount of black liquor recycled, dilution factor, and pulp yield. The result is that for normal kraft pulp yields the flow of weak black liquor or total spent liquor could be as

low as 15,000 lb. per ton pulp or as high as 32,000 lb. per ton pulp. As a guide, the average amount of total spent liquor can be taken to be about 22,500 lb. per ton pulp. Thus a bleach plant effluent flow foreseen as above represents almost twice the flow from a pulp mill. This means that pulp mill spent liquors plus bleach plant effluents (with a volume as foreseen) would represent almost three times the current flow to a pulp mill recovery system. Or, if all of the input water for spent liquor going to a pulp mill recovery system could be derived in effect from bleach plant effluent, pulp mill spent liquor plus excess bleach plant effluent would represent almost twice the current flow to a pulp mill recovery system.

Although the extent to which bleach plant effluent flows can be reduced below 5000 gal./ton pulp remains to be seen, it is likely that further significant reductions will be achieved with the possibility of process modifications such as arising, for example, from high-consistency investigations where chemical reactants are added as gases (3). Process modifications like this are of particular interest to the present project and are considered later in this report.

In discussing the reduction of water input in holopulping (1), attention was drawn to the significance of being able to dewater to a high consistency between chemical process steps. This is considered further in the following.

DEWATERING TO HIGH CONSISTENCY

In mechanical dewatering operations removal of liquor in a screw press is known to give consistencies up to as high as about 40%, whereas a drum washer with press rolls, for example, is capable of giving consistencies of only up to about 15%. Of the two possibilities the first allows for the more complete removal of liquor.

In contemplating the use of presses between stages a number of points arise including whether the press will function satisfactorily with the material to

be fed to it. Other questions would include factors related to arriving at a specific design, for example.

Inquiries revealed that, generally speaking, trials run in screw presses to dewater pulp to high consistency use pulp from existing mills and require a considerable quantity of pulp. Fortunately, a small laboratory screw press was located. It has a small interrupted-flight screw and requires about 2 kg. o.d. pulp for such a test.

Discussions suggested it would be desirable to determine whether chlorine dioxide-alkali pulps are markedly affected by the action of this screw press. To learn what would happen if it were to be used to dewater to high consistency between stages would be of particular interest. However, for this laboratory press it is known that a free stock such as an unrefined kraft pulp can dewater too fast, causing practical difficulties in the use of this press. Thus, it seems likely the same situation probably would be encountered if fiberized chips from the oxidation step, for example, were to be fed to the press. (This behavior of unrefined kraft pulp is unlike that observed in commercial units.) Additionally, some difficulties have been observed in the past with a pulp slipping in this press when alkaline.

Nevertheless, to consider the use of screw presses for dewatering to high consistency, a pulp was prepared using the process conditions set out in Table I. The pulp was fed to the press at 8% consistency, at which essentially no water drained from this holopulp when it was held in hand. No difficulty such as slipping in the press was observed. Fines from the white water were added back to the pulp before evaluation. The results from this evaluation, along with similar test results for the pulp before pressing, are given in Table II.

TABLE I

SCREW PRESSING OF CHLORINE DIOXIDE-ALKALI PULP

Raw material:	Fiberized red maple chips; Code W/PB/1	
Lignin modification:	Consistency, 6.0%	Time, 140 min.
	ClO_2, 9.0%	Temp., 25 → 35°C.
Alkali extraction:	Consistency, 8.0%	Time, 120 min.
	Sodium hydroxide, 9.0%	Temp., 80°C.
	Final pH, 11.1	
Hypochlorite:	Consistency, 12%	Time, 120 min.
	Avail. chlorine, 3.0%	Temp., 40°C.
	Sodium hydroxide, 0.4%	Final pH, 9.5
	Yield, 63.3%	TAPPI brightness, 80.7
	Screening, 98.9% return including 0.3% rejects	

(Note: Pulp screened with no acid wash beforehand and with white water recycle.)

Screw pressing:	(Beloit-Jones Lab. Screw Press)	
	Consistency in, 8.0%	Consist. out, near 25%
	Retaining pressure, 65 p.s.i.	
	No. of cycles: 6 (pulp and white water recombined)	
	Code: 5HCP	

TABLE II

PULP PROPERTIES BEFORE AND AFTER SUCCESSIVE DEWATERING

	Before Pressing					After Pressing				
Pulp	5					5HCP				
Beating time, min.	0	2	4	7	12	0	2	4	6	8
Canadian freeness, ml.	480	410	330	290	190	370	345	290	270[a]	230[a]
Handsheet drainage, sec.	4.6	4.8	5.3	6.8	12.1	5.6	6.8	7.8	10.9	16.1
Density, g./cc.	0.67	0.69	0.70	0.73	0.77	0.75	0.76	0.79	0.80	--
B. smoothness (back), ml./min.	850	620	470	460	460	470	410	450	410	--
Spec. scatt. coeff., 650 mm.	275	270	255	235	200	215	205	175	165	--
Breaking length, km.	6.8	7.3	7.9	8.5	9.1	7.9	8.0	8.7	8.8	--
Stretch, %	2.4	2.6	2.7	3.0	3.0	3.9	3.7	4.0	3.9	--
Tear factor	61	60	63	57	57	65	64	67	61	--
Zero-span breaking length, km.	16	17	17	17	17	16	17	17	17	--
M.I.T. fold	50	80	120	260	580	400	610	1020	1270	--

[a] Fines through freeness pad.

Comparison of the two sets of results in Table II makes it clear that after six passes through the laboratory screw press there were marked changes in pulp properties. It will be seen that handsheet drainage time and sheet density both increased. There is also some analogy to the effects of high-consistency refining in that, for example, tear factor is greater than the original tear and stretch is up by at least 50% (4, 5). It is noted that, in both screw press dewatering and high-consistency refining, mechanical energy is transmitted to the pulp in a semisolid state by a compressive shearing action with fiber-to-fiber rubbing, on which basis a similarity in effect is to be expected.

The influence on pulp properties could be regarded as an advantage or a disadvantage depending upon the product to be made. Thus, in a general sense, since it would be better to have a pulp suited to making as wide a range of products as possible, it appears the use of screw presses could tend to be a factor in limiting the versatility of a bleached hardwood holopulp.

From the standpoint of maintaining versatility of a bleached hardwood holopulp, it appears that the use of screw presses as a means of dewatering to high consistency throughout a complete process could be undesirable. On the other hand, although six passes of a bleached red maple pulp through the laboratory screw press had a significant influence on pulp properties, the following assumption is made. A screw press could be used between lignin modification and alkali extraction to bring the consistency to, say, 20% without the associated compressive shearing action loosening the fiber structure significantly because the fibers are relatively resistant to mechanical force at this point in the process.

OBSERVATIONS ON THICKENING AFTER SCREENING

The next part of the discussion is concerned with observations made when thickening red maple pulps after screening. Because of the possible practical

implications with respect to the use of washers in a holopulping process, these observations are included here.

In Progress Report Twelve (6), where bleached chlorine dioxide-alkali pulps from red maple and aspen were compared, the former were prepared using six chemical process steps including a split lignin modification, whereas the latter were prepared using only three chemical process steps, namely, lignin modification, alkali extraction, and hypochlorite reaction. A desire to use the simpler process in preparing the red maple pulp needed for investigations as discussed already with reference to Tables I and II led to the application to red maple of the process conditions used in the three-stage preparation of bleached aspen pulp. These are the conditions for the first experiment in Table III.

The product from the hypochlorite reaction in this experiment was found to be very difficult to thicken by dewatering on a muslin-covered box after screening. Some indication had been obtained previously that this difficulty could be encountered; however, the experience in this case was markedly more adverse than that encountered when screening either the red maple or aspen pulps referred to in Progress Report Twelve, for example. The exact reason why dewatering was very difficult is not known. It appeared some portion of the pulp, that was possibly pectic in nature, was blinding the muslin as well as sealing off the settled mat of fibers. Loss of material to the white water, which was recycled through the screen, was relatively high at 6.1% when this pulp was screened.

In the earlier work, using six chemical process steps to prepare red maple pulps, thickening after screening was easier. Since perhaps this arose from the use of a higher alkali extraction temperature of 70°C., that was tried in the second experiment in Table III. Although there was a noticeable improvement in thickening after screening, some difficulty was still noted and higher extraction

TABLE III

PULPING PROCESS CONDITIONS AND THICKENING BEHAVIOR OF RED MAPLE CHLORINE DIOXIDE-ALKALI PULP

Material: Fiberized red maple chips; Code W/PB/1

Lignin Modification: 9.0% chlorine dioxide, 3.5% sodium hydroxide, 6% consistency, 25 → 35°C., 140 minutes, final pH 2.7

Alkali Extraction: 9.0% sodium hydroxide, 8.0% consistency, 120 minutes

Expt.	Temp., °C.	Final pH
1	60	11.6
2	70	11.6
3	80	11.0
4	90	10.9

Hypochlorite Reaction: 4.5% avail. chlorine, 0.25% sodium hydroxide, 12% consistency, 40°C.

Expt.	Time, min.	Final pH	Yield, %	Screening Loss, %	Rejects, % o.d.p.	Klason + Acid-Sol. Lignin, %	TAPPI Brightness[a]
1	130	8.8	71	6.1	10.7	7.9	67
2	140	9.0	69	5.4	2.7	7.3	69
3	170	7.9	63	1.3	1.4	2.9	80
4	160	7.8	61	1.0	0.7	-	82

[a] Brightness sheets prepared in distilled water.

temperatures of 80 and 90°C. were considered in a third and a fourth experiment. In both cases, thickening after screening proceeded apparently as for a hardwood chemical pulp. Furthermore, the amount of material lost to the white water was reduced from about 6% to less than 1.5%, screen rejects were at an acceptable level, lignin content decreased by about 4%, and TAPPI brightness increased by about 10 points. On the debit side, net yield was about 3% lower.

It was concluded that the difficulty experienced in thickening by dewatering could be overcome and that a pulp can be prepared from red maple using 9% chlorine dioxide with only three processing steps.

This series of experiments provided the basis for selecting the process conditions used in Table I.

RECYCLING OF CHLORINE DIOXIDE SPENT LIQUOR

Another approach to the reduction of water input in holopulping depends upon whether or not the limited solubility of chlorine dioxide in water is an obstacle. To reduce total water input through reducing water input in an oxidation step of the process, either spent liquor from an aqueous-phase oxidation needs to be recycled through the chlorine dioxide absorber or the oxidation should be carried out at high consistency with the chlorine dioxide added as a gas.

While the second alternative is conceptually more attractive, its realization calls for experimentation with a gaseous chlorine dioxide stream and the development of a suitable high-consistency reactor. Experiments covering this area will be discussed later.

To determine the prospects for recycling chlorine dioxide spent liquor, a primary point is to find the extent to which recycling influences the amount of

oxidant needed to achieve a certain degree of delignification. This requires quantitative addition of chlorine dioxide.

One experimental approach would be to pass a known amount of chlorine dioxide gas into a spent liquor, then trap the amount not absorbed and the amount absorbed could be calculated, irrespective of the degree to which the absorbed gas had reacted with the spent liquor. Another experimental approach would be to add a known amount of chlorine dioxide solution to a spent liquor, but this results in an accumulation of water so that it is necessary to remove water. If evaporation to remove water is accompanied by the loss of a volatile, oxidant-consuming substance, then a correspondingly erroneous result will be obtained. However, in work on evaporation of spent liquor (7) no significant amount of volatile organic substance was detected, and after some reconsideration of the first approach discussed in Progress Report Three (8) the second was chosen.

The procedure followed in recycling spent liquor from an oxidation step, with the addition of chlorine dioxide, is described in the experimental section. From the results for red maple as presented in Table IV it can be seen that with reuse of spent liquor the Kappa number following alkali extraction showed no apparent change.

In view of an earlier opinion that more oxidant was needed when liquors were recycled (8), a question which arises concerns the sensitivity of this approach to revealing whether or not an appreciable amount of oxidant might be consumed by the recycled spent liquor. To resolve this uncertainty, data were obtained as in Table V. From this it can be seen that Kappa number after alkali extraction is a reliable indication of the amount of chlorine dioxide that has reacted during the previous step, whereas that is not the case for Kappa number after chlorine dioxide oxidation.

TABLE IV

RECYCLING CHLORINE DIOXIDE SPENT LIQUOR

Raw Material fiberized red maple chips; Code -/PB

Alkali Conditioning: 2.5% NaOH, 80°C., 30 min., 10% consistency, final pH 9.3

Lignin Modifications: 6.0% ClO_2, 25 → 35°C. in 60 min., 5% consistency. The spent liquor squeezed out after each reaction, usually about 1600 g., was reduced to about 1000 g. in a rotary film evaporator operating at 30 in. Hg and 30°C. and used as the make-up liquor in the next oxidation.

Cycle	0	1	2	3	4	5
Time, min.	80	70	55	50	45	45
Final pH	1.95	1.65	1.55	1.40	1.30	1.30
Kappa no.[a]	72.4	--	--	--	--	73.3

Alkali Extraction: (of washed oxidation stage) 5.5% NaOH, 80°C. for 120 min. at 10% consistency

Cycle	0	1	2	3	4	5
Final pH	10.5	10.5	10.6	10.3	10.4	10.4
Total yield, %	72.3	73.3	73.0	74.0	74.1	73.3
Kappa no.[a]	49.1	44.6	46.3	46.0	45.4	48.0

[a] Of washed sample.

TABLE V

CHLORINE DIOXIDE ADDED VS. KAPPA NO.

Raw Material: fiberized red maple chips; Code -/PB

Alkali Conditioning: 2.5% NaOH, 80°C. for 30 min. at 10% consistency, final pH 9.3

Lignin Modifications: 25 → 35°C. in 60 min., 5% consist.

Code	A	B	C	D	E
ClO_2, %	6.0	5.5	5.0	4.5	4.0
Time, min.	75	70	60	50	45
Final pH	1.9	1.9	2.0	2.1	2.1
Kappa no.[a]	77.0	--	83.4	--	76.2

Alkali Extraction: (of washed oxidation step) 5.5% NaOH, 80°C. for 120 min. at 10% consistency.

Final pH	10.4	10.6	10.9	11.0	11.0
Total yield, %	71.9	72.2	73.5	74.1	77.4
Kappa no.[a]	49.1	52.5	56.7	63.7	70.3

[a] Of washed sample.

In the experiment carried out to obtain the results as in Table IV, the separation of oxidized fiberized chips and spent liquor was accomplished without the addition of any wash water to the spent liquor. This meant about 300 g. per 1900 g. or 16% of the spent liquor was purged from the system in each cycle, as illustrated in Fig. 1.

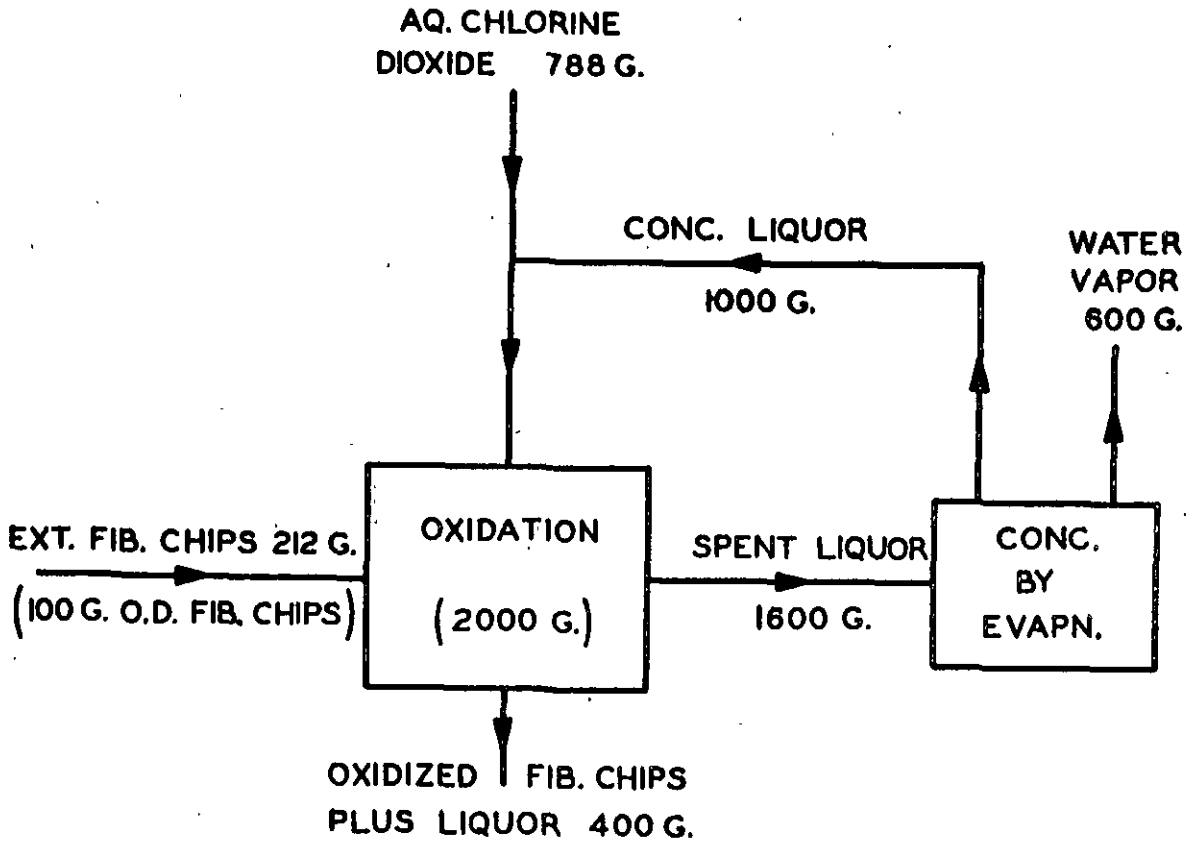


Figure 1. Inputs and Outputs of Aqueous Oxidation with Experimental Spent Liquor Recycle; Compare Table IV

As the experiment proceeded and the number of cycles increased, the final pH of the spent liquor decreased from 1.95 to 1.30 and the time required for the chlorine dioxide to react decreased from 80 to 45 minutes. It appears a steady state had been reached when spent liquor had been recycled for the fourth time.

This is the first occasion in this project when clear evidence has been obtained that the rate of oxidation is significantly influenced by changes in pH. Should optimization of process conditions show a relatively low pH is a disadvantage, for example, with respect to degradation, then pH adjustment with alkali would be necessary.

The results on recycling spent liquor from an aqueous-phase chlorine dioxide oxidation step are interpreted to mean water input could be reduced by liquor recycling without an increase in the chlorine dioxide consumption to achieve a certain degree of delignification. This interpretation also indicates that products of chlorine dioxide degradation which pass into solution during the oxidation are relatively inactive compared with material remaining in the fiberized red maple chips. Although a significant difference in the ability of lignin degradation products in a spent liquor, compared with in oxidized fiberized chips, to consume chlorine dioxide was found previously (9), the realization that the former products are relatively inactive was somewhat unexpected.

REVIEW OF RESULTS

The success achieved in demonstrating that the spent liquor from an aqueous-phase oxidation could be recycled satisfactorily and the consequent impact on water balance are best considered with reference to a complete holopulp process as presented previously in Report Eleven (1). Figure 2, a partial reproduction of a flow diagram from that report, is included here to facilitate discussion.

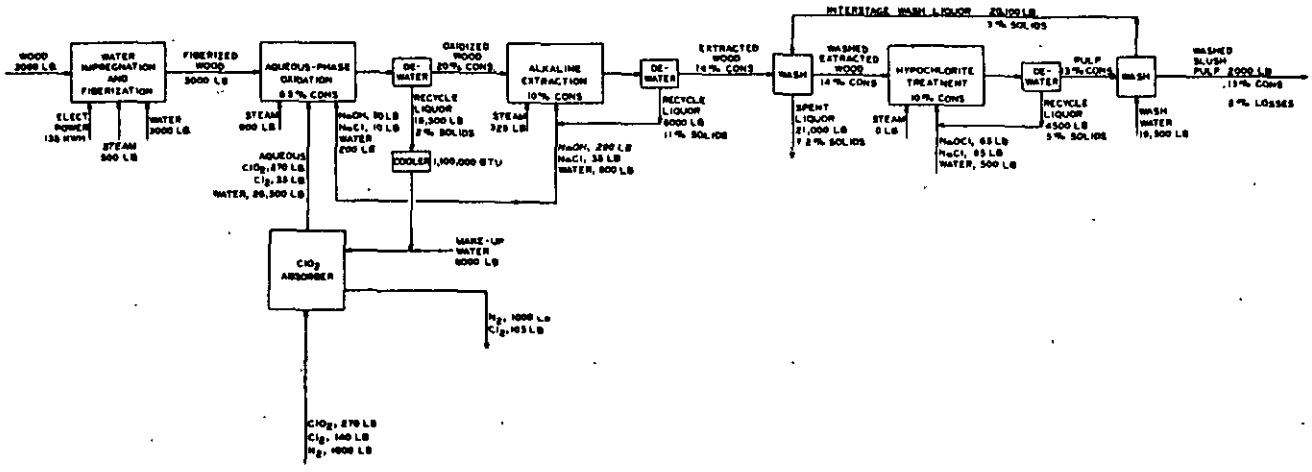


Figure 2. Partial Flow Diagram for Holopulp Process (1)

In this diagram, liquors are shown as being recycled to the aqueous-phase oxidation, alkaline extraction, and hypochlorite treatment. If these liquors were not recycled, the liquor outputs in pounds per ton pulp would be:

Aqueous-phase oxidation	18,500
Alkali extraction	6,000
Hypochlorite treatment	4,500
Spent liquor ex-washer	21,000
Total:	50,000

This total output is more than that discussed above for bleach plant effluents, and over twice the average output quoted for pulp mill spent liquors to a recovery system.

Now, consider Fig. 2 on the following basis:

1. Liquor from the aqueous-phase oxidation can be recycled as shown and confirmed by experiment.

2. Oxidized wood or fiberized chips can be dewatered to 20% consistency as shown and discussed above.

3. Liquor from the alkaline extraction can be recycled as shown.

4. Liquor from the hypochlorite treatment cannot be recycled as shown.

The last assumption acknowledges the possibility that to maintain bleached pulp brightness it is conceivable liquor recycling could be deleterious. At the same time, it is assumed that recycling of liquor from the alkaline treatment would be possible.

On the above basis, liquor outputs in pounds per ton pulp would be:

Aqueous-phase oxidation	nil
Alkali extraction	nil
Hypochlorite treatment	4,500
Spent liquor ex-washer	21,000
	25,500
(Convert to lb./a.d. ton pulp)	
Subtract	2,550
Total:	22,950....say, 23,000.

A total liquor output of 23,000 lb./a.d. ton bleached pulp essentially equals the current average amount of spent liquor flowing from a pulp mill to its recovery system and is only about one third of the flow from a pulp mill plus bleach plant if the latter is put at 42,000 lb./ton pulp. This leaves unresolved a number of points in the flow diagram in Fig. 2, but these are not seen as serious obstacles to the possible success of a holopulping process.

Thus, it is concluded that although the spent liquor stream from a complete holopulping process could be more dilute than from an existing pulp mill, total liquor output is not seen now as a possible roadblock. Furthermore, it is conceivable that effluent output from a holopulping process for producing bleached hardwood pulp could be appreciably less than from a pulp mill plus bleach plant.

HIGH-CONSISTENCY GAS-PHASE OXIDATION

At an earlier date, some experiments using gaseous chlorine dioxide and pin chips were carried out with limited success as discussed in Progress Report Three (8). This approach was abandoned in favor of pursuing that leading to a series of experiments covered in Progress Report Five (10). In those experiments, aspen fiberized chips were used and the oxidation was carried out at high consistency in a laboratory continuous reactor to which was fed a chlorine dioxide-air stream.

Although in the later work (10) some practical difficulties were experienced, especially with the feeder and with measuring the amount of chlorine dioxide consumed, these were in the category of equipment problems. Generally speaking, the experiments were successful. The chemical consumption was comparable to that for analogous experiments with an aqueous-phase oxidation, and the pulps produced were essentially comparable to pulps prepared using an aqueous-phase oxidation (11).

An attractive aspect of reaction at high consistency with gaseous chlorine dioxide added to the surrounding gas phase without the addition of water is the possibility of reducing water input and effluent volume for the pulping process, particularly if aqueous-phase oxidation liquor could not be recycled as was believed to be the case at an earlier date (8). Reduced effluent volume, in this approach, is gained at the expense of needing to strip the chlorine dioxide from the chlorine dioxide-in-water obtained when most of the chlorine is separated from chlorine dioxide in an absorption tower after it comes out of a generator.

If aqueous-phase oxidation liquor can be recycled, as now appears to be the case, the situation is different, as can be seen from the discussion that follows.

GASEOUS-PHASE AND LIQUOR-RECYCLE OXIDATIONS

Considering reaction at high consistency with gaseous chlorine dioxide as an alternative to aqueous-phase oxidation with recycled liquor as in Fig. 2, the amount of heat needed to strip out the chlorine dioxide after separation of chlorine in the absorber could be the main disadvantage. This will be discussed first.

The stripping of chlorine dioxide as represented in Fig. 3 assumes this can be achieved with a steam input equating to the heat needed to raise the temperature of the outgoing water to about 60°C. It is assumed a stripper could be designed so that all of the outgoing water would be essentially free of chlorine dioxide. This means hot water from the stripper would be suitable for use as wash water, make-up water, and dilution water for washed slush pulp, as in Fig. 2. Thus, there would be no need to cool and recycle this water to the absorber.

The advantages of gaseous chlorine dioxide reaction at high consistency, as in Report Five (10), compared with aqueous-phase oxidation with recycled liquor, as in Fig. 2, are listed below.

1. There would be no requirement for steam input (900 lb.) to the oxidation.

2. The need for mechanical dewatering after oxidation would be eliminated.

3. With no liquor to recycle, there would be no associated need for cooling (1.1×10^6 B.t.u.).

4. Assuming hypochlorite treatment without the liquor recycle, as in Fig. 2, 4500 lb. liquor from dewatering after hypochlorite treatment could be recycled to partially lower than consistency before alkali extraction.

5. The make-up water to adjust the consistency to 20% before alkali extraction could be lowered to 3500 lb.

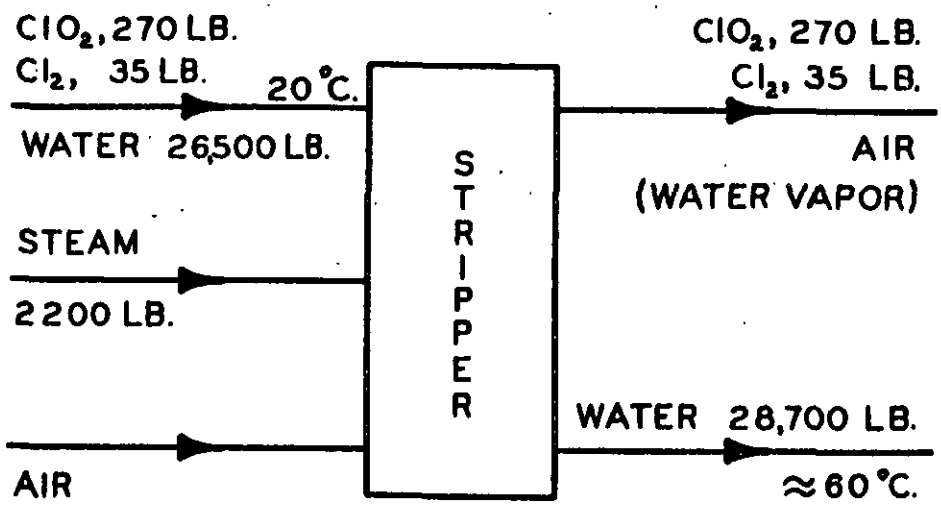


Figure 3. Air Stripping of Chlorine Dioxide-in-Water Assuming Outgoing Water at About 60°C.

6. For hypochlorite treatment without liquor recycle, 4500 lb. of fresh water (e.g., ex-stripper) could be used, giving a total spent liquor flow of 21,000 lb., compared with 25,500 lb.

To summarize the situation at this point, for spent liquor flows in lb. per ton o.d. pulp, three cases will be considered, namely:

I. A process as in Fig. 2, but without recycle of both aqueous-phase oxidation and hypochlorite liquors.

II. A process as in Fig. 2, but without recycle of hypochlorite liquors.

III. A process as in Fig. 2, but without recycle of hypochlorite liquors and with aqueous-phase oxidation substituted by gaseous-phase oxidation (as discussed above).

	I	II	III
Spent liquor ex-washer (Fig. 2), lb.	21,000	21,000	21,000
Aqueous-phase oxidation, lb.	18,500	nil	nil
Hypochlorite treatment, lb.	4,500	4,500	nil
Total, lb./ton o.d. pulp:	44,000	25,500	21,000

Now, accepting that (I) compares unfavorably with either (II) or (III), consider further (II) and (III) in terms of steam requirement differences in lb. per ton o.d. pulp, which would be:

	II	III
Stripper, lb.	--	2200
Oxidation, lb.	900	--
Cooler ($1.50), lb.	say, 3000	--
Evaporators, lb.	1500	--
Difference totals, lb.:	5400	2200
	2200	
Net difference, lb.:	3200	(or $1.60)

The steam requirement for a stripper is based on the situation illustrated in Fig. 3 and steam needed for oxidation follows from Fig. 2. For the cooler, the need to remove about one million B.t.u.'s has been translated into an equivalent amount of steam using the cost bases of $\$1.50/1 \times 10^6$ B.t.u. for chilling and 50¢/1000 lb. for steam (10). The additional 4500 lb. of spent liquor for (II) have been converted to an equivalent steam requirement of 1500 lb. for evaporation, assuming a steam economy of 3.0. In sum, this leads to 3200 lb. more steam, or an equivalent extra cost of $1.60 per ton pulp for (II), which is for a process as in Fig. 2 without recycle of hypochlorite liquors, compared with a similar process having a gaseous-phase oxidation (as discussed above).

Summarizing, (II) and (III) may be compared in terms of differences as follows:

II	III
--	Stripper for ClO_2 gas
Aqueous-phase reactor	High-consistency gas-phase reactor
Mechanical dewatering	--
Liquor cooler	--
Extra steam and cooling (equivalent to 3200 lb.)	--

In a general sense, (II) and (III) appear as possible pulping process alternatives, and it is conjectured that the process in which the oxidation is based on the use of a high-consistency ClO_2/air reactor could be preferred, providing a suitable reactor were to be available.

HIGH-CONSISTENCY GAS-PHASE REACTORS

To help envisage the kind of reactor that might conceivably be used for high-consistency gas-phase oxidation, it is possible to consider a partially analogous situation. This exists in the recent commercial development of oxygen bleaching. In the Kamyr equipment, for example, pulp is fed to a fluffer at the top of a reactor where oxygen and steam are also introduced, as illustrated in Fig. 4. After mixing in the fluffer, the pulp passes down the reactor at high consistency for a controlled retention time before being discharged. To achieve the desired oxygen bleaching reaction, the reactor is operated at 12 atmospheres pressure (12, 13).

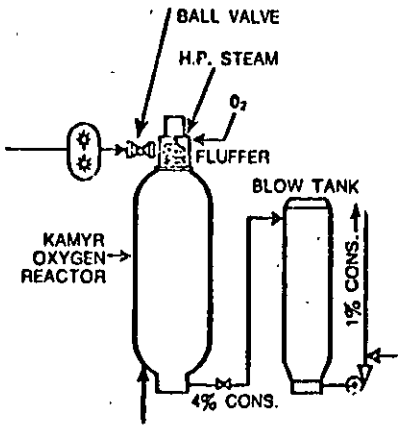


Figure 4. Kamyr High-Consistency Gas-Phase Reactor with Pulp Fed to Fluffer at the Top Where Oxygen and Steam Are Also Introduced

As far as this project is concerned, the important aspects of the development partially illustrated in Fig. 4 would seem to be the fact that there now is equipment available which is capable of:

bringing together high-consistency pulp and gaseous reactant,

mixing the pulp and gaseous reactant,

retaining the bulky mixture during the reaction, and

discharging the reacted pulp.

It is possible to imagine fiberized chips being fed to a fluffer along with a stream of chlorine dioxide with the mixture then held in a reactor for an appropriate time before being discharged.

There would be some important differences such as materials of construction and operation at not more than one atmosphere instead of at 12 atmospheres pressure. Since materials of construction would be relatively expensive, comparatively small reactors as would follow from short reaction times would be a desirable goal.

In the experiments involving gaseous chlorine dioxide reaction at high consistency described in Progress Report Five (10), the temperatures were around

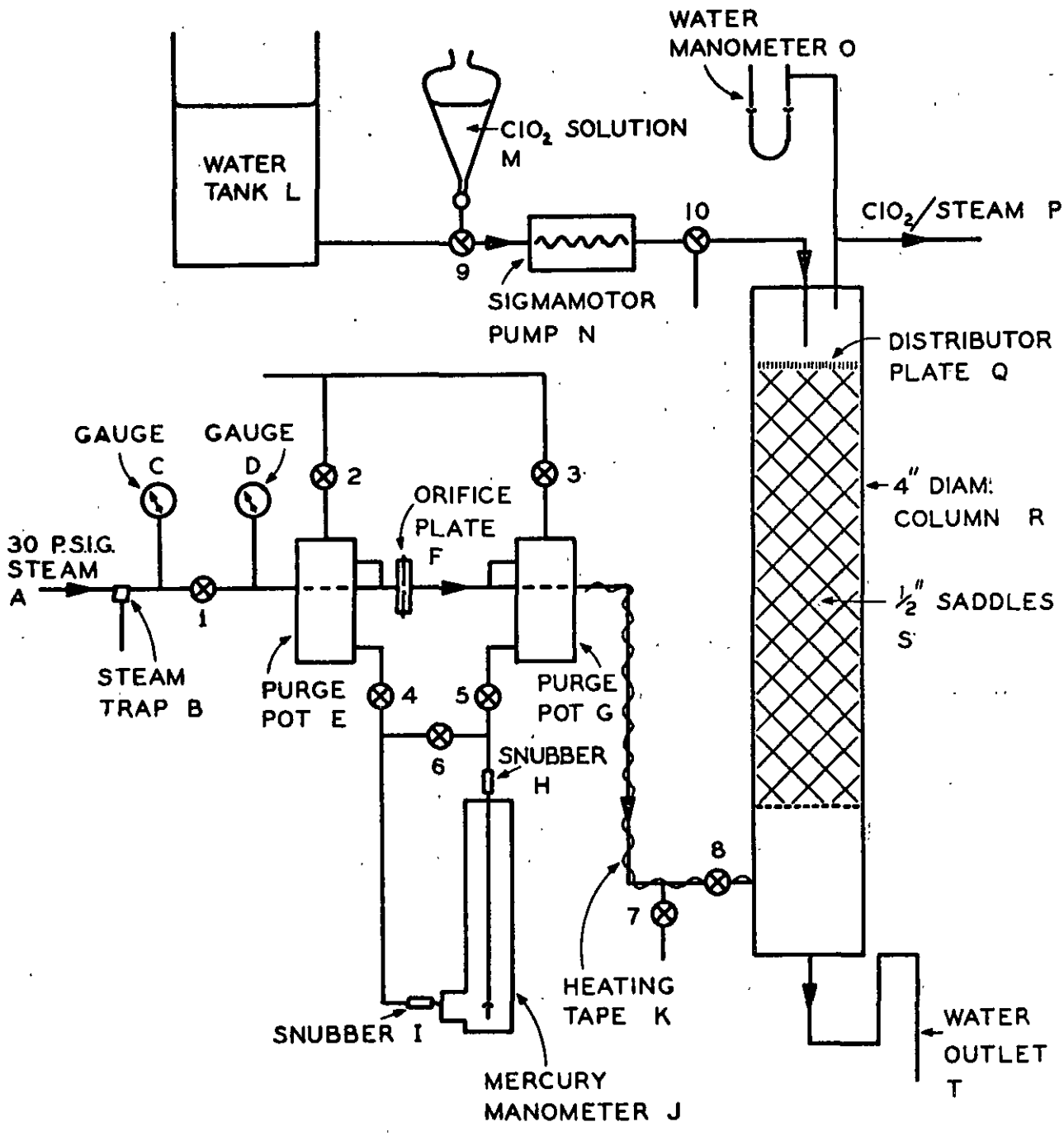
40°C. and reaction times about 30 minutes. This reaction time seemed reasonable, but because of the bulkiness of fiberized chips, a relatively large reactor would be needed.

HIGH-CONSISTENCY GAS-PHASE/STEAM REACTION

While reviewing the idea of conducting high-consistency reactions with gaseous chlorine dioxide at temperatures above 40°C., work described on high-consistency gas-phase bleaching (14) led to the thought of using the gaseous reactant in steam. Assuming a reaction temperature of, say, 90°C. compared with 40°C. as in previous experiments (10), and assuming a doubling of the reaction rate for not more than each ten-degree increment in temperature, the previous reaction time of about 30 minutes would be reduced to not more than a minute.

If this kind of approach proved to be feasible, there are other incentives for pursuing it, as will be discussed later. From a practical viewpoint, the first matter was to bring together fiberized chips and the gaseous reactant in steam in laboratory experiments to obtain more definite knowledge on what happens.

The experimental plan was to produce a stream of chlorine dioxide/steam of known flow rate and composition for batchwise reaction with fiberized chips. For this purpose, a chlorine dioxide steam generator has been constructed as illustrated in Fig. 5.



VALVES

1 NEEDLE

2-8 GATE

9,10 3-WAY

Figure 5. Flow Diagram of Chlorine Dioxide/Steam Generator

When the generator is in operation, essentially the stream (P) of chlorine dioxide/steam is obtained by steam stripping a measured volume of analyzed chlorine dioxide solution (M) delivered at a predetermined rate by a Sigmamotor pump (N) to the stripper column (R). The flow of steam in the stream (P) is regulated by controlling the steam input through Gate Valve 8 to this stripper column (R) by Needle Valve 1. Steam input is determined, knowing the manometer (J) reading across the orifice (F) in the steam line. The needed amount of steam to the column for a particular experiment is calculated knowing the target flows of the chlorine dioxide streams and the characteristics of the system, which have been determined.

Now, consider the volume of chlorine dioxide/steam (with 5% ClO_2) that would need to be delivered to, say, 100 g. fiberized chips in one minute to allow for reaction with 6% chlorine dioxide, as applied in the previously discussed liquor recycle experiments. The required volume would be:

$$\frac{6}{(67.5/18)(0.6)} \times \frac{100}{5}$$

or 53.3 liters/min. (density of steam = 0.6 g./liter). From this volume, it is apparent that the success of reacting fiberized chips with chlorine dioxide/steam will be dependent upon very rapid removal of the chlorine dioxide from the gaseous stream.

The procedure used in the reaction of fiberized chips with chlorine dioxide/steam has been to pass this gas stream over a batch of presteamed, fiberized chips and then to trap the unreacted oxidant in the exit gas. For this purpose, the apparatus, including a steam-jacketed reaction vessel, has been assembled, as illustrated in Fig. 6.

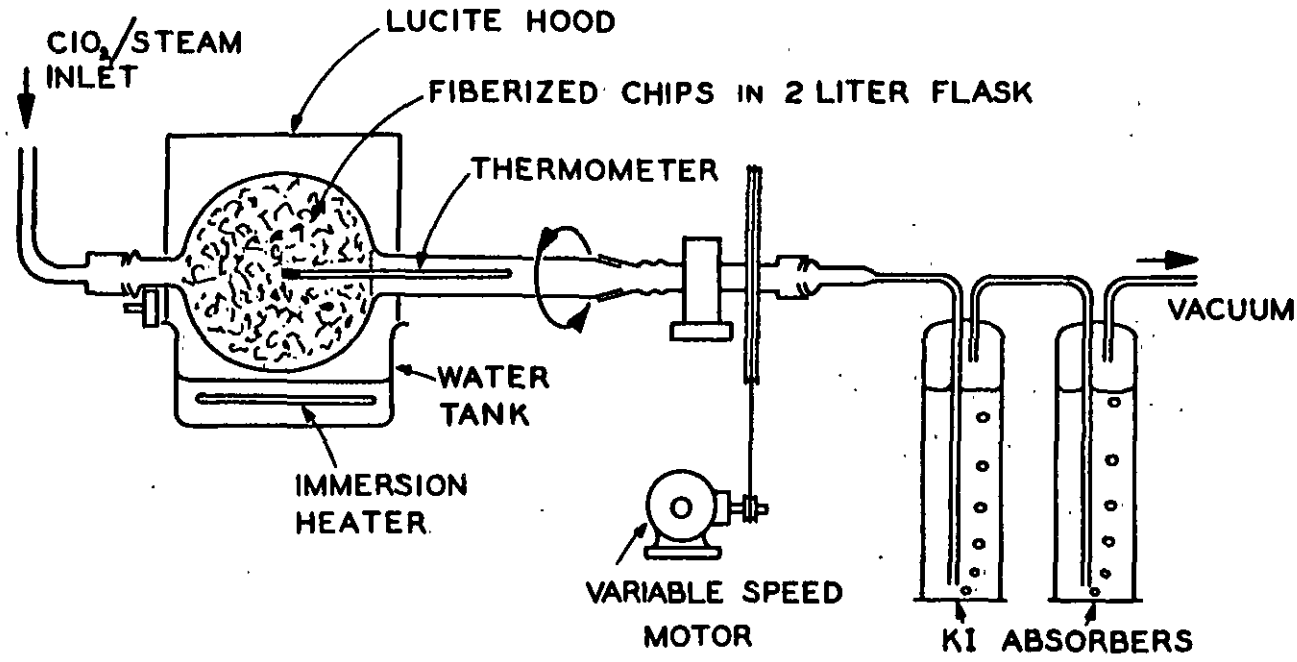


Figure 6. High-Consistency Gas-Phase/Steam Experimental Reactor

The results of experiments conducted using this reactor and its associated chlorine dioxide/steam generator (Fig. 5) are given in Table VI. From this, it can be seen that the moisture content of the fiberized chips ranged from about 10 to 50%. It is anticipated, on the basis of observations during earlier experiments at 40°C. (10), that moisture content influences the reaction.

In the third experiment (Table VI), as soon as the chlorine dioxide/steam flow to the reactor was complete, it was flushed with steam. The chlorine dioxide consumed by the fiberized chips was determined to be 6.2%, or 90% of the total added on the basis of the difference between chlorine dioxide input and the amount collected in the absorbers. Since the total volume of chlorine dioxide/steam passing to the reactor was essentially 43 liters, this means that in 1.7 min. the total volume of the reactor could have been displaced once in every 5 seconds with only 10% of the incoming chlorine dioxide passing through unreacted. In view of the

TABLE VI

HIGH-CONSISTENCY CHLORINE DIOXIDE/STEAM REACTIONS

Raw material: fiberized red maple chips, Code -/PB

Alkali pretreatment: 2.5% NaOH, 80°C., 30 min., 10% consistency, final pH 9.3

Chlorine dioxide oxidation: 100-102°C.

Run no.	01	02	03
Pulp charge, g.[a]	33.9	57.5	55.0
Moisture content, %[b]			
Before	9.2	43.0	51.4
After	--	--	53.5
ClO_2 applied, %	7.5	8.0	6.9
ClO_2 consumed, %[c]	4.1	5.7	6.2
Gas volume, with 4 v/v % ClO_2, liters	--	--	43
Gas flow time, min.	1.0	1.9	1.7
Dwell time, min.	ca. 3	ca. 3	0
Total reaction time, min.	4	5	1.7

[a] Equivalent ovendry original fiberized material.

[b] Wet basis.

[c] Calculated from applied less amount in KI absorbers.

fact that there was no mechanical mixing of the chlorine dioxide/steam and fiberized chips, this is a remarkable situation.

With this limited practical knowledge of what happens, it is possible to envisage more clearly fiberized chips being fed to a fluffer along with a stream of chlorine dioxide/steam and, in a matter of seconds, the chlorine dioxide would be removed from the steam and consumed by the fiberized chips. Presumably, the dwell time in a reactor could be very brief, which is an important factor regarding its design, relative size, and cost.

Before proceeding to discuss other process implications of these experiments, it is appropriate to comment further on the runs as in Table VI. It was observed after Run 03, for example, when looking at the reactor from the inlet end, that all of the material appeared to have been uniformly reacted, whereas, when looking at the reactor from the outlet end, it was obvious that channeling had occurred so that some material was comparatively unchanged. In addition, it could be seen that in zones where gas had reacted, larger bundles of fibers apparently had been completely penetrated by the chlorine dioxide.

If the reaction were to proceed via diffusion-controlled absorption of chlorine dioxide in the moisture which is present, it was previously pointed out that, as the temperature is increased above, say, 40°C. to, say, 90°C., the relatively greater rate of the chemical reaction mechanism could lead to increasingly less uniform reaction across fiber bundles. The nature of the observations made at the present time on chlorine dioxide/steam reactions suggests the possibility of chemisorption or some other phenomenon being a significant factor in the reaction mechanism.

Now that it is possible to perceive more positively the feasibility of high-consistency gas-phase/steam oxidations, it will be necessary to improve the

experimental procedure so as to achieve more uniform reaction within the reactor and to permit evaluation of this approach. For the present, it is appropriate to consider briefly the broader implications of success.

A considerable incentive to pursuing high-consistency gas-phase/steam oxidation in a holopulping process would come from being able to use the stream of gas from a chlorine dioxide generator.

If the chemical equivalent of chlorine contained in the chlorine dioxide could be used equally effectively, the nominal capacity of the chlorine dioxide plant would be reduced.

In earlier work (15), it was shown that chlorine dioxide-in-water containing 15 $^{w}/_{w}$ % chlorine could be substituted for the chemical equivalent amount of chlorine dioxide. This would reduce the size of a 50-ton-per-day chlorine dioxide plant to:

ClO_2: 47 t.p.d.

Cl_2: 8 t.p.d.

Where the generator is producing a gas of relative chlorine dioxide: chlorine composition in the ratio 100:80, and if this gas could be used instead of one with 85:15 composition, this would reduce the size of a 50-ton-per-day chlorine dioxide plant to:

ClO_2: 38.5 t.p.d.

Cl_2: 31 t.p.d.

The resultant reduction in capital cost has been estimated to be \$1.3 x 10^6. There would also be a considerable reduction in daily operating costs including:

Electrical power (100,000 kw.-hr., a.c.)	500
Electrode maintenance ($120)	120
Steam (225 tons)	225
Total:	845

This would represent a reduction in pulp cost of at least $1.7 per ton (assuming 500 t.p.d.) without allowance for reduction in capital.

In Report Eleven (1), such advantages of using generator gas were pointed out, except that the chlorine dioxide-chlorine gas stream was envisaged as being diluted with air. Subsequent inquiries have made it apparent that steam could be the diluent gas.

Thus, the possibility is envisaged of material being fed to a fluffer along with a stream of chlorine dioxide-chlorine/steam direct from a generator with a reaction time in the order of a few seconds.

CHLORINE DIOXIDE-ALKALI PULPING WITH LESS OXIDANT

At an earlier date, consideration was given to chemical impregnation or chemical pretreatment of chips before fiberization and delignification. As a result, aspen chips impregnated in a liquor containing sodium hydroxide and sodium sulfite were fiberized at near-atmospheric pressure. Exploratory chlorine dioxide-alkali delignification included the preparation of Pulps CP/At-1 and CP/At-2 in Table VII using "CP" to indicate chemical pretreatment and "At" to designate fiberization at near 1 atmosphere. Complete details are given in Appendix I.

Apart from there being sulfur in the liquor system, these results were of interest in that they indicated that the amount of chlorine dioxide needed for delignification apparently could be reduced. However, evaluation of the pulps to give data as included in Table VII revealed that the bleached pulp (CP/At-2) beat rapidly and provided handsheets with relatively high sheet density.

Arising from the later demonstration that temperature when fiberizing is a factor influencing sheet density as illustrated, for example, by the results obtained for Pulp P in Report Twelve (6), and outlined here in Table VII, chemically impregnated chips were fiberized at a higher pressure than in earlier experiments. Subsequent delignification gave bleached Pulp CP/P-3 (Table VII). This was prepared after fiberization as for Pulp P except that chlorine dioxide addition was a nominal 6%. As in the case of Pulp P, Pulp CP/P-3 gave handsheets of significantly lower density than for Pulp CP/A-2, as shown in Table VII.

In pursuing the possibility of reducing chlorine dioxide addition to, say, 6%, experiments were carried out on red maple chips fiberized in a Bauer pressurized refiner using conditions to give W/PB/2 as in the Experimental section and discussed again later. The amount of alkali added before and after chlorine dioxide reaction

TABLE VII

ASPEN PULP PREPARATION PROCEDURES AND EVALUATION DATA
AS DETAILED IN APPENDIX I

	CP/At-1	CP/At-2	CP/P-3	P
Impregnation	liquor			water
Fiberization	≈1 atm.		71 p.s.i.	
Lignin modification, % ClO_2	6[a]	4 + 2[a]	6.0[a,b]	9.0
Alkali extraction, % NaOH	5[a]	3.5 + 1.5[a]	9.0[a]	9.0
Hypochlorite, % available Cl_2	nil	4.4[a]	4.5[a]	4.5
Yield, %	73[a]	64[a]	64[a]	67
Bleached	no	yes		
Beating time, min.	0	0	0	0
	3	2	2	2
	5	4	7	8
	8	6	11	16
	13		18	24
Canadian freeness, ml.	155	80	450	610
	130	75	380	560
	120	75	310	460
	102	60	250	320
	85		155	165
Handsheet drainage, sec.	n.d.	n.d.	4.9	4.3
	n.d.	n.d.	5.7	4.7
	n.d.	n.d.	6.4	5.1
	n.d.	n.d.	7.7	6.2
	n.d.		16.6	13.5
Handsheet density, g./cc.	0.556	0.730	0.640	0.610
	0.583	0.770	0.657	0.634
	0.587	0.799	0.689	0.677
	0.619	0.811	0.690	0.722
	0.643		0.722	0.758

[a] Calculated on o.d. weight of unwashed fiberized chips.

[b] Hot-water solubles, 12% removed before lignin modification.

was varied as in Table VIII. A temperature of 80°C. was selected following the observations as discussed in connection with Table III.

For a total addition of 9.5-16.5% alkali, the yield after alkali extraction varied only from 66 to 70%. TAPPI brightness reached 80 after reaction with hypochlorite and forming brightness sheets from water. It should be noted that these pulps appear whiter to the eye than would be expected for an 80 TAPPI brightness. This is because the unbeaten pulp brightness tabs are appreciably bonded with the result that there is more transmittance of light than usually occurs in determining unbeaten pulp brightness.

Red maple pulp preparation procedures and pulp evaluation data set out in Table IX include two bleached pulps, namely Pulps W/PB-6B/1 and W/PB-6B/2, representing essentially the upper and lower levels of alkali used in Table VIII. This, in turn, leads to a change in the amount of hypochlorite needed to obtain a bleached pulp[a].

It is clear from Table IX that bleached pulps can be obtained using 6.0% chlorine dioxide.

The process conditions for Pulp W/PB-6B/1 compared with Pulp W/PB-6B/2 lead to the former's beating more rapidly to smoother handsheets of greater density. Pulp W/PB-6U/2, which is the unbleached form of Pulp W/PB-6B/2, beat significantly less rapidly and bulkier handsheets were obtained.

The conditions for fiberization in a Bauer pressurized refiner were based on the conditions previously used in an Asplund machine which had been found to lead

[a] It is noted that the codes used in Table IX relate to process conditions as follows: W/P represents water impregnation (W) before pressurized fiberization (P) in either a Bauer (W/PB) or Asplund (W/PA) pressurized refiner using 6 or 7.5% chlorine dioxide (W/PB-6, etc.) to give a bleached (B) or unbleached (U) pulp (W/PB-6B, etc.) in Experiment no. 1, etc. (W/PB-6B/1, etc.).

TABLE VIII

CHLORINE DIOXIDE-ALKALI DELIGNIFICATION OF RED MAPLE WITH ADDITION OF 6% CHLORINE DIOXIDE

Alkali conditioning: Temperature 80°C., consistency 10%, time 60 min.

	A	B	C_1	C_2	C_2	D_1	D_2	D_2	E_1	E_1	E_2	E_2
Sodium hydroxide, %	7.5	7.0			5.0					4.0		
Final pH	11.7	11.6			11.1					10.2		

Lignin modification: Temperature 25 → 35°C., consistency 10%, chlorine dioxide 6.0%.

Time, min.	70	75			80					80		
Final pH	2.0	2.1			1.9					2.0		

Alkali extraction: Temperature 80°C., consistency 12%, time 120 min.

	A	B	C_1	C_2	C_2	D_1	D_2	D_2	E_1	E_1	E_2	E_2
Sodium hydroxide, %	9.0	8.0	7.0	6.5		6.0	5.5		6.5		5.5	
Final pH	11.9	11.7	11.7	11.5		11.4	11.3		11.5		11.2	
Yield, %	66.3	67.4	68.5	69.1		69.5	70.2		68.4		69.2	
Screen rejects, estd. %						14-16						
Scr. rej. after PFI, % o.d.p.	0.4	0.4	0.2	0.6		0.3	0.4		0.6		0.5	

Hypochlorite: Temperature 40°C., consistency 20%.

	A	B	C_1	C_2	C_2	D_1	D_2	D_2	E_1	E_1	E_2	E_2
Available chlorine, %	--	--	--	3.0	4.5	--	3.0	4.5	3.0	4.5	3.0	4.5
Sodium hydroxide, %	--	--	--	0.3	0.4	--	0.3	0.4	0.3	0.4	0.3	0.4
Time, min.	--	--	--	75	150	--	55	120	75	105	65	105
Final pH	--	--	--	9.4	8.6	--	9.4	8.9	9.5	8.6	9.5	8.7
TAPPI brightness, %	--	--	--	72	80	--	70	79	71	79	69	77

TABLE IX

RED MAPLE PULP PREPARATION PROCEDURES AND PULP EVALUATION DATA
AS DETAILED IN APPENDIX II

Pulp	W/PB-6B/1	W/PB-6B/2	W/PB-6U/2	W/PB-7.5B	W/PA-7.5B[a]
Impregnation	water				
Fiberization temp./press.	158°C./70-1 p.s.i.				
Machine	B				A
Minutes at pressure	5.0				4.3-5.6
Alk. conditioning, % NaOH	7.0	4.0		1.0	
Temperature, °C.	80			70	
Lignin modification, % ClO_2	6.0			7.5 (2 stages)	
Alkali extraction, % NaOH	8.0	5.0		8.2 (2 stages)	
Hypochlorite, % available Cl_2	3.0	4.5	nil	3.0	
Yield, %	62	64	69	64	66
TAPPI brightness (water)	78	75	n.d.	n.d.	81
Beating time, min.	0	0	0	0	0
	2	2	2	2	3
	4	4	4	4	6
	6	8	10	10	10
	10	12	16	22	22
Handsheet drainage, sec.	5.2	4.5	4.2	5.2	4.7
	5.8	4.8	4.3	5.3	4.9
	6.3	5.3	4.4	5.5	4.8
	6.9	6.8	5.5	6.0	5.3
	10.2	10.3	12.1	10.1	11.5
Handsheet density, g./cc.	0.706	0.670	0.576	0.682	0.594
	0.722	0.711	0.592	0.696	0.614
	0.734	0.733	0.629	0.706	0.644
	0.747	0.709	0.673	0.724	0.656
	0.766	0.733	0.743	0.774	0.739
Bendtsen smoothness, ml./min.	996	1490	2130	1950	1630
	945	1180	1660	1410	1510
	943	1070	1500	1250	1080
	824	1360	1390	1210	900
	813	1260	1560	1030	900

[a] Further details under Pulp Vb, Table XIII, Report Twelve (6).

to the best bleached pulp properties (6). These properties are illustrated in Table IX under Pulp W/PA-7.5B. It was found that both Pulps W/PB-6B/1 and W/PB-6B/2 had handsheet densities higher than for Pulp W/PA-7.5B, which was not in accord with expectation. This difference in density must be a reflection of process conditions.

To discern that part of the process with which this difference may be associated, Pulp W/PA-7.5B can be compared with Pulp W/PB-7.5B. Regarding their preparation, this differs only in that two different machines, namely Asplund and Bauer, were used to fiberize chips. Thus, apparently, translating results obtained using one machine to the use of another is not as straightforward as was hoped. It is assumed that optimization of process conditions would give a bleached pulp comparable to Pulp W/PA-7.5B using only 6.0% chlorine dioxide in one stage.

The water impregnation-fiberization-alkali conditioning sequence of steps in the process as applicable in Table IX functions so as to separate chips into fiber bundles and remove some alkali-soluble material. To obtain the cost benefit of using less oxidant, it seems likely that the function of alkali should be exercised before the addition of oxidant.

Knowing the process conditions in Table IX, it should be possible to carry out chip impregnation with alkali instead of water to simplify the process by the omission of alkali conditioning after chip fiberization. This is supported by the data in Table VII for Pulp CP/P-3.

Thus, it is assumed that optimization of process conditions would give a bleached hardwood pulp using only 6.0% chlorine dioxide in one stage. The process steps could be as in Fig. 2 except that chips are envisaged as being treated with alkali before fiberization.

For 500 tons of pulp per day, changing the basis for chlorine dioxide needed from 7.5 to 6% and assuming these could be as the chemical equivalent of chlorine dioxide plus chlorine in the weight ratio of 85:15, the chlorine dioxide plant production would go from:

$$\left.\begin{array}{l} ClO_2: \ 47 \text{ t.p.d.} \\ Cl_2: \ \ 8 \text{ t.p.d.} \end{array}\right\} \quad \text{to} \quad \left\{\begin{array}{l} ClO_2: \ 37.5 \text{ t.p.d.} \\ Cl_2: \ \ 6.5 \text{ t.p.d.} \end{array}\right.$$

Now if, instead of 6% chlorine dioxide, the chemical equivalent of chlorine dioxide plus chlorine in generator gas with the composition of 100:80 could be used, the chlorine dioxide plant would produce:

ClO_2: 31 t.p.d.
Cl_2: 25 t.p.d.

This most favorable situation would lead to substantial savings in chemical and capital costs as previously estimated.

EXPERIMENTAL

RAW MATERIALS

Red Maple

The red maple (Acer rubrum L.) chips were from the same supply as described in Report Twelve (6) with the screened chips having an initial content of 35.2% wet basis and a density of 31.5 lb. (o.d.)/cu. ft. green.

Aspen

Chemically impregnated aspen (Populus tremuloides Michx.) chips were obtained from the in-feed chute of the Bauer primary refiners in a chemigroundwood mill similar to one described by Richardson and LeMahieu (16). The chips, sampled during normal operating conditions, had been impregnated at atmospheric pressure and 80°C. with the chemical uptake being about 1.4% on the o.d. wood for both NaOH and Na_2SO_3. These chips were designated CP.

A sample of fiberized, impregnated chips was obtained from the out-feed chute of the Bauer primary refiners of the same mill as where the impregnated chips were sampled. The refining was carried out at near-atmospheric pressure with a 0.025-in. disk gap, and the chips were fed to the refiner at about 60% consistency. The collected material had a Canadian freeness of 515 ml. and gave a Bauer-McNett classification as in Table X and was designated CP/At.

CHIP FIBERIZATION

Both the red maple chips and the chemically impregnated aspen chips were fiberized in the no. 418 Bauer pressurized refiner at The Bauer Bros. Co., Springfield, Ohio, as for the loblolly and black spruce chips described in Report

TABLE X

BAUER-McNETT CLASSIFICATION DATA FOR CP/At[a]

On 6 mesh, %	1.3
On 12 mesh, %	7.6
On 35 mesh, %	30.9
On 65 mesh, %	25.1
Through 65 mesh (by difference), %	35.1

[a] Water temperature, 17°C.

Thirteen (17). About half of the red maple chips were impregnated with water as described in Report Thirteen. The fiberization data are given in Table XI.

CHLORINE DIOXIDE-ALKALI DELIGNIFICATIONS

Aqueous Chlorine Dioxide in the Lignin Modification Stage

All reactions were carried out in plastic bags with the products being mixed at regular intervals. Alkali conditioning (where included), lignin modifications, alkali extraction, and hypochlorite bleaching (where included) were carried out under conditions as recorded in the tables. After each reaction, the products were well washed with deionized water. Dewatering was effected using a laundry-type spin drier with the products being contained in a nylon cloth bag. Whether or not the reacted products were given an acid soak using dilute HCl at a pH of 4 for 30 minutes at room temperature is given in the tables.

Chlorine Dioxide/Steam in the Lignin Modification Stage

The alkali conditioning in Table VI was carried out as described above with the reacted products being washed with deionized water. A description and

TABLE XI

NO. 418 BAUER FIBERIZATION DATA[a]

Species	Red maple			Aspen
Code	-/PB	W/PB/1	W/PB/2	CP/P
Chip treatment[b]	R	I	I	C
Moisture content, % wet basis	28.5	59.2	58.5	60.8
Fiberization				
Steam pressure, p.s.i./°C.	70/158	70/158	70/158	70/158
Steaming time, min.	2.50	2.50	5.00	5.00
Plate clearance, 0.001 in.	35	35	35	35
Run time, min.	6.11	5.71	9.50	5.95
Feed rate, o.d. tons/day	5.50	4.37	5.03	5.81
Load, brake h.p. days/o.d. ton[c]	3.07	4.13	3.70	1.46
Bauer-McNett classification, %[d]				
On 6 mesh	42.9	21.9	17.6	9.3
On 12 mesh	15.5	21.6	16.6	15.7
On 35 mesh	20.4	27.2	30.8	35.0
On 65 mesh	9.2	10.7	14.4	18.7
Through 65 mesh (by difference)	12.0	18.6	20.6	21.3

[a] Each run was made with the equivalent of about 45 lb. o.d. chips.

[b] R = raw or untreated, I = water impregnated, C = impregnated with $NaOH/Na_2SO_3$ solution.

[c] These values should be increased 20% to obtain the estimated total, including allowances for no load and motor efficiency.

[d] Water temperature 16-18°C.

method of operation for the chlorine dioxide/steam generator and the gas-phase reactor is given in the discussion on high-consistency gas-phase/steam reaction. The alkali-conditioned fiberized chips were passed through a fluffer several times to remove any lumps before being carefully placed in the 2-liter reaction flask. The flask was rotated at about 18 r.p.m. during each run to help secure uniformity of reaction between the chlorine dioxide and fiberized material.

SCREENING

When carried out, screening was done in a pulsating flat-bed screen fitted 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.

PULP EVALUATION

The pulp evaluation data were obtained as described in Report Twelve (6) with the exception that the Bendtsen smoothness determinations were made on the 1.2-g. handsheets.

CONCLUSIONS

On the basis of experiments described and discussed in this report, conclusions as listed below have been reached.

1. Total liquor output from a complete holopulping process is not seen as a possible roadblock, although the spent liquor stream could be more dilute than in an existing chemical pulp mill.

2. It seems that the spent liquor or effluent output from a holopulping process for producing bleached hardwood pulp could be appreciably less than from a pulp mill plus bleach plant.

3. There is a firmer basis to foresee fiberized material being fed to a fluffer and reacted with a stream of chlorine dioxide/steam in a relatively short time, which which opens the way for the possible direct use of a chlorine dioxide-chlorine/steam generator gas and the lowering of costs.

4. Bleached hardwood holopulps can be obtained using as little as 6% chlorine dioxide in one stage and thereby providing substantial savings in chemical and capital costs as previously estimated, the envisaged process being based on chip impregnation with alkali, chip fiberization, chlorine dioxide oxidation, alkali extraction, and hypochlorite reaction.

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APPENDIX I. DATA ON ASPEN USING LESS OXIDANT

TABLE XII

PREPARATION OF ASPEN PULPS WITH CHEMICAL PRETREATMENT OF CHIPS

Material	CP/At[a]		CP/P[a]	([b])
Hot water extraction: 70°C., 30 min.				
Final pH	n.a.	n.a.	7.8	n.a.
Yield, %[c]	n.a.	n.a.	88.2[d]	n.a.
Lignin modification: 25 → 35/40°C. in 60 min., consistency 6%.				
ClO_2, %	6.0	4.0	6.0	9.0
NaOH, %	--	--	2.3	3.5
Time, min.	270	150	145	210
Final pH	1.8	2.2	3.1	2.7
Yield, %	85.3	85.5	--	--
Alkali extraction: 60°C., consistency 8%.				
NaOH, %	5.0	3.5	9.0[e]	9.0
Time, min.	10	10	120	120
Final pH	11.8	11.3	11.9	11.5
Yield, %	73.1	74.6	--	--
Lignin modification: 2% ClO_2, 25 → 40°C. in 60 min., consistency 12%.				
Time, min.	n.a.	127	n.a.	n.a.
Final pH	n.a.	2.6	n.a.	n.a.
Yield, %	n.a.	72.9	n.a.	n.a.
Alkali extraction: 1.5% NaOH, 60°C., 10 min., consistency 12%.				
Final pH	n.a.	10.0	n.a.	n.a.
Yield, %	n.a.	68.8	n.a.	n.a.
Hypochlorite bleach: 40°C., consistency 12%.				
Av. Cl_2, %	n.a.	4.4[f]	4.5	4.5
NaOH, %	n.a.	0.4	0.25	0.25
Time, min.	n.a.	120	170	190
Final pH	n.a.	7.9	8.9	8.0
Yield, %	n.a.	64	63.6[g]	67.4[h]
Screen rejects, % o.d.p.	n.a.		1.1	0.2
Screening loss, % o.d.p.			3.5	0.9
Brightness, % (H_2O)	n.a.	72.0[i]	78.1	75.5
Brightness (EtOH)	n.a.	81.4[i]	82.5	80.8
Pulp code	CP/A[t]-1	CP/A[t]-2	CP/P-3	P

Note: See footnotes on next page.

TABLE XII (CONTD.)

PREPARATION OF ASPEN PULPS WITH CHEMICAL PRETREATMENT OF CHIPS

[a] See Experimental.

[b] Water-impregnated aspen chips, fiberized in OVP Asplund at 71 p.s.i. for 4.3 to 5.6 min. with 0.016-in. gap. See Table X, Report Twelve (6).

[c] All percentages quoted are based on the original o.d. fiberized material unless stated otherwise.

[d] A cold-water extraction gave a yield of 88.7%.

[e] 80°C. extraction.

[f] Alkali-extracted pulp screened with rejects given 600 counter revs. in TAPPI disintegrator and rescreened to give 5.7% o.d.p. screen rejects. Both accepts combined and centricleaned in Bauer no. 600 centricleaner using 1/8-in. dia. exit and 42 p.s.i. inlet pressure. Twelve-percent rejects obtained. Centricleaned accepts used for bleaching.

[g] Given a dilute HCl soak for 30 min. at pH 4. Note: this yield is complicated by the fact that the original fiberized material had a significant amount of inorganic matter in it; see footnote (e) for cold-water-extraction yield.

[h] Soaked in SO_2 water for 30 min. at pH 3.5-4.

[i] A sulfurous acid treatment (1% SO_2, 30°C., 90 min., 12% consistency) gave brightness values of 75.6 (H_2O) and 84.9 (EtOH).

TABLE XIII

HANDSHEET DATA FOR ASPEN PULPS AS IN TABLE XII

Pulp code	CP/A-1					CP/A-2			
Beating time, min.[a]	0	3	5	8	13	0	2	4	6
Canadian freeness, ml.	155	130	120	102	85	80	75	75	60
Handsheet drainage time, sec.	--	--	--	--	--	--	--	--	--
Handsheet density, g./cc.	0.556	0.583	0.587	0.619	0.643	0.730	0.770	0.799	0.811
Bendtsen smoothness, ml./min.	3190	3180	2870	2650	2480	2440	1690	1360	1240
Spec. scattering coeff., cm.^{2}/g.	254	241	249	226	212	143	131	123	116
Breaking length, km.	6.49	7.37	7.42	8.22	8.66	9.32	9.76	10.2	10.7
Stretch, %	2.0	2.3	2.2	2.1	2.3	2.8	2.7	2.7	2.6
Tear factor	72.0	65.0	62.9	63.3	61.8	56.4	49.7	49.5	51.2
Zero-span breaking length, km.	14.5	14.5	15.2	15.0	16.5	16.0	17.3	17.4	17.7
M.I.T. fold	132	192	256	400	540	1200	1630	1630	1830

Pulp code	CP/P-3					P				
Beating time, min.[a]	0	2	7	11	18	0	2	8	16	24
Canadian freeness, ml.	450	380	310	250	155	610	560	460	320	165
Handsheet drainage time, sec.	4.9	5.7	6.4	7.7	16.6	4.3	4.7	5.1	6.2	13.5
Handsheet density, g./cc.	0.640	0.657	0.689	0.690	0.722	0.610	0.634	0.677	0.722	0.758
Bendtsen smoothness, ml./min.	1890	2060	1690	2240	1910	1950	1520	885	762	826
Spec. scattering coeff., cm.^{2}/g.	218	213	197	192	158	246	249	243	214	181
Breaking length, km.	7.19	7.63	8.64	9.22	9.77	6.09	6.94	7.91	9.18	9.74
Stretch, %	2.4	2.6	2.6	2.8	2.6	1.8	2.1	2.3	2.5	2.4
Tear factor	67.5	68.2	64.1	62.5	57.4	62.6	64.1	57.0	56.8	50.2
Zero-span breaking length, km.	16.7	16.3	18.0	18.0	17.6	14.1	14.3	15.8	16.9	16.6
M.I.T. fold	65	86	193	235	495	21	26	64	182	387

[a] Valley beater bedplate weight 2.0 kg.

APPENDIX II. DATA ON RED MAPLE USING LESS OXIDANT

TABLE XIV

PREPARATION OF RED MAPLE PULPS WITH LESS OXIDANT

Ref.	ClO_2, %	NaOH, %	Cl_2, %	Temp., °C.	Time, min.	Consist., %	Final pH	Yield, %	TAPPI Brightness
Alkali conditioning									
1[b]	--	7.0	--	80	60	10	11.6	88.1	--
2[b]	--	4.0	--	80	60	10	10.3	91.9	--
3[b]	--	1.0	--	70	10	6	8.8	n.d.	--
Lignin modification: 25 → 35°C. in 60 min.									
1	6.0	--	--		75	10	2.0	85.6	--
2	6.0	--	--		60	10	2.0	n.d.	--
3	4.97	--	0.88		60	6	2.0	n.d.	--
Alkali extraction									
1	--	8.0	--	80	120	12	11.8	65.1	--
2 (W/PB-6U/2)	--	5.5	--	80	120	12	11.1	69.0	n.d.
3	--	5.0	--	70	20	10	9.4	n.d.	--
Lignin modification: 25 → 35°C. in 60 min.									
1	n.a.	--	--		--	--	--	--	--
2	n.a.	--	--		--	--	--	--	--
3	2.53	--	0.45		90	10	2.5	n.d.	--
Alkali extraction									
1	--	n.a.	--		--	--	--	--	--
2	--	n.a.	--		--	--	--	--	--
3	--	2.7	--	70	20	15	10.1	69.2	--
Hypochlorite bleach									
1 (W/PB-6B/1)	--	0.3	3.0	40	150	20	8.7	61.7	82.3[c] (78.3)[d]
2 (W/PB-6B/2)	--	0.4	4.5	40	120	20	n.d.	64.4	81.5 (74.9)
3 (W/PB-7.5B)[e]	--	0.8	3.0	40	65	15	9.4	53.5	n.d.

[a] All percentages quoted are based on the original o.d. fiberized material unless stated otherwise.

[b] Starting material W/PB/2, see Table XI.

[c] Ethanol.

[d] Water.

[e] Prior to the reaction with hypochlorite, this pulp was given a dilute HCl soak for 30 min. at pH 4 and 20°C. followed by 15 sec. at 25% consistency and 3.4 kg./cm. load in a PFI mill before screening. Screen rejects were 1.3% o.d.p. and screening loss was 2.9% o.d.p. Only the screened material was reacted with hypochlorite.

Note: Pulps W/PB-6B/1, W/PB-6U/2, and W/PB-6B/2 were not screened nor treated with dilute acid at any stage.

TABLE XV

HANDSHEET DATA FOR RED MAPLE PULPS AS IN TABLE XIV

Pulp code	W/PB-6B/1					W/PB-6B/2				
Beating time, min.[a]	0	2	4	6	10	0	2	4	8	12
Canadian freeness, ml.	325	290	230	185	150[b]	410	370	290	220	150[b]
Handsheet drainage time, sec.	5.2	5.8	6.3	6.9	10.2	4.5	4.8	5.3	6.8	10.3
Handsheet density, g./cc.	0.706	0.722	0.734	0.747	0.766	0.670	0.711	0.733	0.709	0.733
Bendtsen smoothness, ml./min.	996	945	943	824	813	1490	1180	1070	1360	1260
Breaking length, km.	8.41	8.74	9.19	9.44	9.73	7.05	7.46	8.28	8.59	9.23
Stretch, %	2.8	2.7	2.9	2.8	2.8	2.7	2.7	2.9	2.9	2.6
Tear factor	63.4	60.9	61.7	60.1	58.5	57.2	54.4	56.3	52.0	50.7
Zero-span breaking length, km.	16.3	17.1	17.6	17.5	17.9	--	--	--	--	--

Pulp code	W/PB-6U/2					W/PB-7.5B				
Beating time, min.[a]	0	2	4	10	16	0	2	4	10	22
Canadian freeness, ml.	620	505	420	245	130[b]	480	440	405	330	225
Handsheet drainage time, sec.	4.2	4.3	4.4	5.5	12.1	5.2	5.3	5.5	6.0	10.1
Handsheet density, g./cc.	0.576	0.592	0.629	0.673	0.743	0.682	0.696	0.706	0.724	0.774
Bendtsen smoothness, ml./min.	2130	1660	1550	1390	1560	1950	1410	1250	1210	1030
Breaking length, km.	5.16	6.17	6.86	8.11	8.93	7.89	8.05	8.13	8.67	9.57
Stretch, %	1.7	2.2	2.4	2.5	2.6	2.7	2.7	2.7	2.7	2.9
Tear factor	64.2	61.6	63.0	55.2	50.1	59.2	57.2	58.0	58.2	53.1
Zero-span breaking length, km.	--	--	--	--	--	13.9	14.2	14.2	14.0	15.1

[a] Valley beater bedplate weight 2.0 kg.

[b] Fines evident in freeness effluent.