Rapid caustic extraction of chlorinated pulp

J. A. Histed and R. Vega Canovas

Histed is senior research associate and Canovas is senior research engineer at CIP Research Ltd., Hawkesbury, Ontario, Canada K6A 2H4.

ABSTRACT *Up to 94% of the lignin that can be removed in the first caustic extraction stage of a conventional process can be removed rapidly from well-chlorinated pulp with two countercurrent displacements with caustic. The time per displacement can be as short as 1.7 s. A slight loss in extraction efficiency is more than made up by improved washing efficiency. On a commercial scale, the chlorinated pulp can be formed into a sheet, washed, extracted twice, and washed three times on a six-stage horizontal washer. Caustic requirements are 2/3 that of a conventional extraction. Energy requirements are lower than in a conventional bleachery. This technology also presents an opportunity to lower the capital cost of a bleachery.*

KEYWORDS
Alkali extraction
Bleaching
Delignification
Energy
Kraft pulps
Stock preparation
Washing

Rapson (*1*) proposed a dynamic bleaching process in which a complete bleaching sequence, such as DEDED, could be carried out by passing chlorine dioxide and caustic solutions alternatively through a pulp mat. He obtained times as short as 2 min for the extraction stages in this process and 19 min for the complete sequence. It was suggested that the process could be carried out on a moving belt or wire. This would require a machine with about 20 times the capacity of modern horizontal washers. However, Brinkley (*2*) modified the process to utilize a series of radial diffusion washers which ultimately developed into the Kamyr displacement bleach plant.

Liebergott (*3*) disclosed a rapid extraction of pulp obtained by mixing caustic with the pulp in a steam mixer at 4–12% consistency followed by pressing to high consistency in less than 1 min.

Axegard (*4*) has shown that the first caustic extraction stage is composed of a rapid reaction and a slow reaction, where the rapid reaction is promoted by high temperature, high alkalinity, and high chlorination levels.

Our laboratory studies into the stoichiometry and kinetics of the first extraction stage (*5*) suggested that the kinetics of the rapid phase of caustic extraction might be fast enough to be carried out on a washer. We also recognized that poor washing after a first extraction stage in conventional bleacheries was a major cause of high bleach chemical consumption. This was even more evident in displacement bleacheries with no wash between the E stage and a succeeding displacement D stage.

Multistage horizontal washers presented a means of carrying out a rapid-displacement extraction as well as a way of correcting the problem of high chemical consumption due to poor washing.

At CIP Research Ltd., we were well aware of the washing capabilities of horizontal washers. The first two multistage horizontal washers in our industry were installed in our pilot plant in Gatineau, Que., in 1967. Based on experiments carried out on these washers, Ontario Paper Co. installed the first commercial horizontal washer in 1973 for red liquor recovery in its Thorold, Ont., sulfite plant (*6–8*). Several other horizontal washers of this design have been installed in sulfite plants in a number of countries.

The wire on these first horizontal washers was carried on a rubber drainage belt, which precluded its use in bleacheries. However, at the time we became interested in rapid displacement caustic extraction, a horizontal washer without a rubber drainage belt was being fabricated for our now defunct sulfite mill in Hawkesbury, Ont.

If chlorination-stage washing, rapid extraction, and extraction-stage washing could all be carried out on one multistage horizontal washer, this would lower the capital cost and energy consumption in a bleachery. Tuomi (*9*) had similar ideas with respect to rapid extraction, except he proposed using two-stage Profeed washers for the first and second extraction stages of a [(C+D)EDED] bleachery.

Preliminary experiments carried out on a Buchner funnel established the feasibility of rapid caustic extraction by displacement. An apparatus was then designed to permit simulation of a horizontal washer.

I. The effects of chlorination level and number of consecutive E stages on extraction efficiency

Chlorination		Single rapid E stage		Double rapid EE stages		Conventional E stage	
Kappa factor	(CD) kappa no.	Kappa no.	E stage efficiency, %	Kappa no.	EE stage efficiency, %	Kappa no.	E-stage efficiency, %
0.166	17.6	7.60	80.6	6.60	88.7	5.20	100
0.199	15.7	5.40	85.8	5.10	88.3	3.70	100
0.232	11.0	4.47	88.2	4.15	92.6	3.60	100
0.265	9.1	3.90	88.1	3.50	94.9	3.20	100

Unbleached pulp: kappa no. = 30.8, viscosity = 33 mPa·s.
Chlorination: 3.0% consistency, 40°C, 7% replacement of Cl_2 with ClO_2.
Conventional E: 3.0% NaOH on Pulp, 11% consistency, 70°C, 1 h.
Single rapid extraction: 6.0% NaOH on pulp, 1.2:1 wash ratio at 11% consistency, 80°C, 20 s per displacement.
Double rapid extraction: 4.2% NaOH in E_1, 10.4% NaOH on pulp in E_2, 1.2:1 wash ratio at 11% consistency, 80°C, 20 s per displacement.

II. The effect of washing on the total kappa number of material leaving an (E+O)-stage commercial washer

Kappa no. of pulp	Kappa no. of pulp plus carryover	Kappa no. of pulp as % of total
2.21	2.55	87
2.86	3.63	79
3.17	3.82	83
3.29	3.63	91
3.34	3.79	88
3.39	5.26	64
3.50	4.34	81
3.57	4.47	80
3.99	5.38	74
4.32	5.00	86
Average 3.36	4.19	81

III. The effect of temperature on displacement washing and extraction stages

Temp. of E and W stages, °C	Total time of forming* + six displacements, s	Average time per displacement, s	(CD)EE kappa no.	Hypochlorite at 70% brightness, % Cl_2 on pulp
20	69	9.9	4.18	1.05
30	50	7.1	4.00	1.10
40	49	7.0	4.07	1.06
50	45	6.4	3.56	0.81
60	36	5.1	3.60	0.84
70	36	5.1	3.42	0.86
80	31	4.4	3.36	0.76
90	31	4.4	3.32	0.77

*Forming time was approximately the same as the time per displacement.
Unbleached pulp: kappa no. = 29.2, viscosity = 28.2 mPa·s.
Chlorination: 7.64% Cl_2 + 0.2% ClO_2 on pulp, 45°C, 3.0% consistency, 2 h, 6.9 kappa no.
Extraction: basis weight = 2.5 o.d. kg/m², vacuum = 10 kPa, wash ratio = 1.25:1 at 8% consistency, 3.0% NaOH in E_1 and 7.0% NaOH on pulp in E_2, three extraction-stage wash displacements (F, W, E, E, W, W, W).
Hypochlorite: 10% consistency, 80°C, 6 min.

(at 94.9% efficiency) could be lower than the total kappa number of pulp plus carryover from a conventional (E+O)-stage washer, where the kappa number of the pulp represents 64–91% of the total kappa number discharged from that washer. This requires a high chlorination level.

The effect of temperature on the time required for sheet formation, a single chlorination stage wash, two stages of extraction, and three wash stages after extraction is shown in **Table III**. At a basis weight of 2.5 kg/m², this entire process took 69 s at 20°C and only 31 s at 80°C. The (CD)EE kappa number and the hypochlorite consumed to reach 70% brightness both approached a minimum at 80°C.

Table IV shows the effect of basis weight on the time required for sheet formation, chlorination stage wash, two extraction stages, and three extraction wash stages. At a basis weight of 1 kg/m² each of the two extraction displacements took 1.7 s. Because of the time required to load the second E stage and wash liquors into the funnel, at which time no displacement was taking place, the total elapsed time that the pulp was in contact with caustic was 14.3 s. At a basis weight of 4 kg/m², the pulp was in contact with caustic for 37.2 s. Basis weight and the length of time in contact with caustic had no effect on the [(C+D)EE] kappa number, the hypochlorite consumption to 72% brightness, or the viscosity at 72% brightness.

The results obtained from a simulation of the flowsheet in Fig. 2 are shown in **Table V**. Aliquots from a single batch of chlorinated pulp were used for all nine cycles. Steady state with respect to the caustic content of the wash trays was reached after about seven cycles. A make-up of 2.0% NaOH on pulp was sufficient to keep the total alkali in the system in balance. There was no systematic change in the [(C+D)EE] kappa no. or viscosity between Cycle 1 and steady state. This pulp required 3.0% NaOH on pulp in a conventional extraction stage, as shown in Table I.

This process is more efficient than conventional extractions with respect to caustic consumption because, in the process described in Fig. 2, a preliminary extraction is carried out using recycled filtrate containing caustic and sodium salts of weak organic acids. The carboxyl groups in chlorinated pulp are all in the hydrogen form. These ions exchange readily with sodium salts and do not require fresh caustic as in conventional extraction. Similar caustic savings can be achieved in a conventional bleachery by the Papricycle process, where washed

IV. The effect of basis weight in displacement washing and extraction stages

Basis weight, o.d. kg/m²	1.0	2.0	2.5	3.0	4.0
Sheet thickness during washing, mm	11	20	25	29	40
Total time, forming + displacements,[a] s	11.6	26.4	32.4	47	88
Average time per displacement, s	1.7	3.8	4.6	6.7	12.6
Time with pulp in contact with NaOH,[b] s	14.3	...	18.8	19.6	37.2
(CD)EE Kappa no.	3.60	3.55	3.47	3.47	3.56
Consumed at 72% brightness, % Cl_2 on pulp	0.75	0.83	0.78	0.72	0.79
Viscosity after H stage, mPa·s	16.0	17.0	16.7	16.9	16.0

[a]Formation time was approximately the same as the time per displacement.
[b]Total elapsed time from start of E_1 to start of wash, this includes time required to load the E_2 and wash liquors into the apparatus between the displacement stages.
Unbleached pulp: Kappa no. = 29.2, viscosity = 28.2 mPa·s.
Chlorination: 7.64% Cl_2 + 0.2% ClO_2 on pulp, 2.5% consistency, 2 h, 45° C, kappa no. 6.1.
Extraction: Sheet formed from 2.5% consistency to ~ 8% consistency, followed by WEEWWW at 13.5-kPa vacuum and a 3-S thickening at 27 kPa. Wash ratio was 1.25:1 at 8% consistency. 3% NaOH was applied in E_1, and 7% NaOH on pulp was applied in E_2. (In a countercurrent process, this requires 2.0% make-up NaOH to maintain steady state.)
Hypochlorite: 10% consistency, 80° C, 6 min.

V. Simulation of the flowsheet (in Fig. 2) using a wash ratio of 1.3:1

Cycle no.	1	2	3	4	5	6	7	8	9
Tray 13 residual, % NaOH on pulp*	0.1	0.4	0.4	0.2	0.5	0.2	0.1	0.2	0.1
Tray 14 residual, % NaOH on pulp	4.2	5.3	6.0	5.6	5.3	4.7	4.5	4.6	4.7
Tray 15 residual, % NaOH on pulp	8.0	7.0	6.0	6.4	6.4	6.0	6.6	6.6	6.7
Tray 16 residual, % NaOH on pulp	...	...	0.2	0.3	0.2	0.4	0.4	0.5	0.3
Shower 4 NaOH, % on pulp	3.8	4.2	5.3	6.0	5.6	5.3	4.7	4.5	4.6
Shower 5 NaOH, % on pulp	10.2	10.0	9.0	8.0	8.4	8.4	8.0	8.6	8.6
Shower 6 NaOH, % on pulp	...	...	...	0.2	0.3	0.2	0.4	0.4	0.5
(CD)EE viscosity, mPa·s	23.5	22.9	22.7	22.6	22.0	22.7	22.6	22.9	22.6
Total alkali at start of cycle	14.0	14.2	14.3	14.2	14.3	13.9	13.1	13.5	13.7
Total alkali at end of cycle	12.2	12.3	12.2	12.3	11.9	11.1	11.5	11.7	11.7

*Tray 13 is the E stage sewer.
Unbleached pulp: kappa no. = 30.8, viscosity = 33 mPa·s.
Chlorination: 6.62% Cl_2 + 0.2% ClO_2 on pulp, 2.5% consistency, 40° C, 90 min.
Extraction: 90° C, 11% consistency. At cycle 1, 3.8% NaOH on pulp was applied at shower 4 and 10.2% NaOH on pulp was added at shower 5. In all further cycles, 2.0% NaOH on pulp was added as make-up.

chlorinated pulp is mixed with extraction-stage filtrate and is then washed on a second washer prior to a conventional extraction stage (*10*).

Reuse of the extraction-stage filtrate on a conventional chlorination washer does not necessarily save caustic, because the reaction products in the sheet are carried back into the extraction stage where they consume fresh caustic (*10*). This type of recycle also increases the carryover of colored material into later bleach stages and increases hypochlorite and/or chlorine dioxide consumption.

Experience gained by simulation of the flow sheet in Fig. 2 showed that we were washing more than necessary ahead of the extraction but that there was dissolved colored matter in the extracted pulp leaving the washer. This was corrected by eliminating one of the two wash stages after chlorination and adding a third wash stage after extraction. This preferred process was used to obtain the results shown in Tables III and IV.

In combination with simplified bleaching (*11-13*), the [(C+D)EE(HD)] sequence was used to bleach northern softwood kraft to 90%+ ISO brightness at a viscosity of 16 mPa·s. The [(C+D)EE(HD)] sequence gave 91%+ ISO brightness at a viscosity of 20 mPa·s. The latter sequence would require a chlorination-stage tower, a six-stage horizontal washer, an 8 min hypochlorite tube, an 8 min D_1 tube, a 2 min E_2 tube, and a 4 h D_2 tower plus washer for implementation on the mill scale. Capital costs would be much lower than for a conventional bleachery.

Conclusions

Others have shown that the caustic extraction stage is composed of a fast reaction and a slow reaction. This work shows that the fast reaction is much faster than has previously been demonstrated.

The rapid-displacement extraction process works best with highly chlorinated pulp.

This process could be implemented in conjunction with simplified bleaching to decrease the capital cost of a bleachery for kraft market pulp. It would also decrease caustic requirements and electrical energy.

Thorough washing after the extraction stage is much more important than has been previously recognized.

Literature cited

1. Rapson, W. H. and Anderson, C. B., Tappi 49(8): 329(1966).
2. Brinkley, A. W., Jr., Nelson, G. G., Jr., Campbell, R. T., and Goff, O. M., U.S. Patent 3,575,795 (April 20, 1971).
3. Liebergott, N., U.S. Patent 3,874,992 (April 1, 1975).
4. Axegard, P., Svensk Papperstid. 82(12): 361(1979).
5. Taylor, R. A., Vega Canovas, R., and Histed, J. A., 1982 International Pulp Bleaching Conference Proceedings, TAPPI PRESS, Atlanta, p. 107.

6. White, J., Canadian Pulp & Paper Industry 31(10): 24(1978).
7. Sexton, E. A., U.S. Patent 4,014,736 (March 29, 1977).
8. Sexton, E. A., U.S. Patent 4,046,621 (Sept. 6, 1977).
9. Tuomi, A., U.S. Patent 4,529,479 (July 16, 1985).
10. Berry, R. M. and Fleming, B. I., Presented at the 1987 Spring Conference CPPA Technical Section Pacific Coast and Western Branches, CPPA, Whistler, B.C.
11. Histed, J. A., Pulp Paper Can. 85(6): T156(1984).
12. Histed, J. A. and Vega Canovas, R., Pulp Paper Can. 88(2): T35(1987).
13. Histed, J. A., U.S. Patent 4,238,281 (Dec. 9, 1980).

The authors wish to thank the management of CIP Research Ltd. for permission to publish this paper, and G. Martel and A. Beaulne for skillful assistance with the experimental work. The efforts of R. C. Reid-Bicknell Engineering Ltd. in designing the horizontal washer are especially appreciated.

Received for review June 12, 1987.

Accepted Oct. 8, 1987.

Presented at the 1987 Pulping Conference.

FROM THE JOINT TEXTBOOK COMMITTEE OF THE PAPER INDUSTRY

Volume 3 of Pulp and Paper Manufacture, Third Edition. Secondary Fibers and Non-Wood Pulping

Edited by M.J. Kocurek, F. Hamilton and B. Leopold

Volume 3 is an in-depth textbook on two important topics: **Non-Wood Pulping** and **Secondary Fibers.**

Chapters combine scientific principles with practical operations, and are grouped under the two main subjects. In Non-Wood Pulping, there are chapters on the history of paper and the importance of non-wood plant fibers, data on and future of non-wood plant fibers, and separate chapters on bagasse, bamboo, cereal straw, reeds, and a fiber that is currently of great interest, kenaf. The final chapters briefly cover papyrus, cotton linters, flax, esparto, jute, sabai grass, hemp and corn stalks. In Secondary Fibers, twelve chapters deal with: secondary fibers and recycling, sources, contaminants, consumption and use, economics, processes and equipment, pulping systems, ink removal, flotation deinking, cleaning and screening, bleaching, and process and quality control.

1987. Book.
Order Number: 02 02 MS03
Price: $57.50
(No member discount)

TAPPI PRESS • Publication Sales
Technology Park/Atlanta • P.O. Box 105113
Atlanta, GA 30348-5113 • (404) 446-1400