

Kraft pulping of coastal softwood from British Columbia using AQ and a digester additive

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BRITISH COLUMBIA HAS ADOPTED regulations limiting the discharge of AOX (adsorbable organic halide) to less than 1.5 kg/metric ton of pulp produced beginning in January 1996. Skeena Cellulose Inc. (SCI) is investigating technologies that will help meet the regulations without significant capital investment. Beyond the immediate environmental issue, the mill is also investigating strategies to reduce production costs and to extend the supply of wood raw materials.

INTRODUCTION

Conventionally cooked kraft pulps contain a small amount of lignin that cannot be removed without severe reduction in pulp yield and strength. This lignin is removed in a subsequent bleaching operation using chlorinated chemicals. These chemicals, especially chlorine dioxide, tend to be expensive, and some form unwanted chlorinated organic compounds. To reduce the formation of these compounds, the bleaching process can be altered to accommodate such nonchlorinated oxidizing agents as hydrogen peroxide, ozone, and oxygen.

Another way of reducing the level of chlorinated organic compounds in the bleachery effluent is to reduce brownstock lignin content by prolonging the cook. However, extended delignification normally reduces yield and produces pulp of inferior quality. Extending the pulping process also results in lower

selectivity of delignification. Extended kraft pulping can be modified by using additives such as anthraquinone (AQ), sodium borohydride, and polysulfides to maintain yield and pulp strengths. Although some of these additives increase yield, the high cost and their effect on pulp quality have precluded their use on a commercial scale. Of these additives, AQ has been shown to preserve pulp strength and increase yield.

Many studies on kraft pulping have been conducted with AQ and solubilized AQ. An internal study by Repap has shown that AQ assists in preserving pulp yield while accelerating the delignification rate. Under the same cooking conditions, kraft-AQ pulp showed a 4.3-unit reduction in kappa number for predominantly coastal chips (approximately 70% hemlock-fir) from British Columbia (BC), with a corresponding increase in lignin-free yield of about 0.9% based on oven-dry (o.d.) wood. Work with chips from the interior of BC (mainly spruce-pine) showed a 6.8-unit reduction in kappa number, with an increase in lignin-free yield of 0.7%. In both cases, the AQ dosage was 0.05% on o.d. wood. Pulps produced from the coastal chips showed an increase in tear strength of 11% but a decline in tensile strength of 3%, with both properties measured at 500-mL CSF. In contrast, pulp produced from interior chips showed a decrease of 5% in tear, while tensile increased by 9% at 500-mL CSF. The overall strength factor (tear x tensile)

ABSTRACT

The effect of anthraquinone (AQ) and digester additive on kraft pulping and bleaching operations was investigated. Extended delignification (kappa no. 25.9) with AQ produced a pulp with good strength and a lower bleaching demand, which reduced the discharge of adsorbable organic halide. Delignification to the normal target (kappa no. 32.7) with AQ increased bleached-pulp yield with no adverse effect on pulp bleachability or brightness development. Kraft-AQ pulps also required less refining energy to achieve the same freeness as a conventional kraft. Kraft-AQ pulps had lower tear strength and higher tensile strength than the conventional kraft at a given level of freeness.

Application:

Results from an operating kraft mill demonstrate the wide-ranging benefits of AQ.

was similar for both coastal and interior chips at all levels of freeness tested.

MacLeod *et al.* (1) studied the application of AQ for a wide variety of softwood and hardwood species. Their results showed an accelerated rate of lignin removal for both kraft-AQ and soda-AQ pulps. At comparable kappa numbers, the unbleached yields were always higher for kraft-AQ pulps than for the equivalent conventional kraft pulp. The strength properties of unbleached kraft-AQ pulps were also equivalent to the kraft pulps for both softwood and hardwood pulps, except for spruce, where tear strength was lower by 10%.

McDonough and Herro (2) examined the effect of AQ and effective alkali charge on the bleachability of conventional, low-lignin softwood and kraft-AQ pulp. Their work showed that effective alkali charge

had relatively little effect on the bleachability of the pulp, but the addition of 0.1% AQ during pulping gave a small but significant reduction in bleached brightness.

Several other authors also have studied the effect of AQ during pulping (3–7). The objective of the present work was to evaluate the effect of AQ on the digester and bleach-plant operations. Delignification was extended to kappa no. 25.9 with AQ during the first part of the trial. The conventional kappa-number target of 32.7 was used throughout the remainder of the trial, which involved the use of AQ or AQ plus a digester additive designed to increase penetration of white liquor into the chips. Chemical consumption in the digester and the bleach plant were monitored along with lignin-free pulp yield, finished pulp quality, and AOX discharges in the treated bleach-plant effluent.

PROCESS DESCRIPTION

Pulping

The pulping area of the A mill at SCI comprises two identical, continuous, single-vessel hydraulic Kamyr digesters installed in 1966. The design capacity for the digesters is 394 air-dried (a.d.) metric tons/day, while the stream rate is 427 a.d. metric tons/day.

Stock from the digester is blown into blow tanks. Pulp from the blow tanks is pumped to the primary knotters (Ingersoll Rand Hi-Q Model B), with the rejects going to the secondary knotters (Johnson). The accepts from the primary and secondary knotters go to the brownstock washers, while rejects from the secondary knotter are blown back to the digester chip bin.

Pulp from the knotters is washed in series on two drum washers (Ingersoll Rand coru-dek), each equipped with end valves and measuring 4.1 m in diameter by 7.9 m in length. The washed pulp is stored in

SPECIES MIX, %		
Species	Control period (Jan. 1995)	Trial period (Feb. 1995)
Hemlock–fir	70 ± 3	68 ± 4
Spruce–pine	26 ± 3	27 ± 3
Cedar–hardwood	4 ± 2	5 ± 2
<i>n</i> *	10	15

**n* = number of tests

I. Species mix in wood chips before and during the mill trials

CHIP CONTENT, %			
Condition	Control period (Jan. 1995)	Trial period (Feb. 1995)	Comments
Bark	1.6	1.8	Visual assessment of condition
Rot	2.3	1.6	Visual assessment of condition
Oversize	1.0	1.0	>45 mm (round hole)
Overthick	4.3	3.5	>10 mm (bars)
Accepts	84.7	89.5	7 mm < x < 45 mm (round hole)
Pins	9.0	5.6	3 mm < x < 7 mm (round hole)
Fines	0.9	0.7	<3 mm (round hole)
<i>n</i>	8	16	Number of tests

II. Chip analysis before and during the mill trials

two high-density storage tanks. Pulp from the brownstock high-density storage is then transferred to three pressure screens (Ingersoll Rand 212 Centrisorter). Primary and secondary rejects are transferred to 212 and 210 Centrisorter screens, with the tertiary rejects going to a rejects refiner (Sprout–Waldron). The screened pulp is washed on another end-valve-equipped drum washer (Ingersoll Rand coru-dek) measuring 4.2 m in diameter by 7.9 m in length. The washed pulp is stored in a screened high-density storage.

Bleaching

Pulp from the screened high-density storage is pumped to a five-stage bleach plant with a bleaching sequence of X(C+D)(EOP)DED. (X represents an enzyme-bleaching stage in screen high-density storage.) All bleach washers (Ingersoll Rand) are 4.2 m in diameter by 7.9 m in length. Pulp is transported using thick-stock pumps (Sunds), with one MC (medium-consistency) pump (Ahlstrom) feeding the first extraction stage.

The first extraction stage has an oxygen-retention tube with the pressure maintained at 138 kPa at the top. The first chlorine dioxide stage also has a retention tube with a MC mixer (Sunds). The second chlorine dioxide stage has a chlorine dioxide mixer (Ahlstrom) with an upflow tower discharging into a retention tower. The pulp from the last stage discharges into two high-density storage tanks. Stock from the storage tanks is transferred to the bleach-plant cleaning system.

TRIAL METHOD

Both digesters are controlled by the distributed control system (DCS), which maintains the digester level, cook *H*-factor, and EA (effective alkali) residual. The strategy of the three control loops is to ensure that the discharge kappa number is as close to the target kappa number as possible.

Screened chips measuring about 8-mm thick by 64 mm in length, consisting predominantly of hemlock–fir, are fed to the digester via a

Condition	CONTROL PERIOD	TRIAL PERIOD (FEB. 1995)		
	(Jan. 1995) K-32.7	2/2–2/10 KAQ-18	2/11–2/20 KAQ-32.7	2/21–2/26 KAQ/add-32.7 ^a
Kappa number (blow line)				
Target	32.7	25.9	32.7	32.7
Actual	31.8	26.7	31.4	31.8
Digester pulping conditions				
Chip meter, rpm	12.6	12.7	13.4	13.8
H-factor	504	615	582	478
Upper cook temp., °C	131	134	133	131
Lower cook temp., °C	153	156	156	154
Sulfidity(TTA), %	28.3	27.8	28.7	27.8
EA, % on o.d. wood	14.3	14.2	14.7	14.3
White-liquor flow, L/min	1048	1052	1079	1083
EA, g/L	84.0	83.2	82.9	81.9
EA (residual), g/L	12.3	11.5	11.4	11.9
Weak black-liquor solids, kg/a.d. metric ton	1794	1839	1764	1727
Weak black-liquor solids, %	19.2	19.5	19.3	19.2
Blow-line screening, %	2.1 ^b	2.8 ^c	3.7 ^c	4.3 ^c
Digester steam conditions				
75-psi steam, kg/a.d. metric ton brownstock	332	280	310	251
175-psi steam, kg/a.d. metric ton brownstock	1355	1366	1319	1314
Total steam, kg/a.d. metric ton brownstock	1687	1646	1629	1565
Yield				
Bleached-pulp hemicellulose, % ^d	14.6	15.2	15.3	15.1
Brownstock, metric tons/day/rpm ^e	34.8	34.7	35.6	35.5
Bleached pulp, metric tons/day/rpm ^e	31.5	31.4	32.3	32.2
Brownstock yield, %	47.7	47.7	48.8	49.2
Bleached-pulp yield, %	43.0	43.0	44.3	44.5

^a Digester additive was Pulp Aid 2M
^b Blow-tank discharge
^c Blow-line sample without knots
^d Measured according to TAPPI T 235 cm-85
^e Chip meter rpm

III. Pulping conditions and yields before and during the mill trials

chip bin and a steaming vessel. Table I shows the wood species analysis for the trial period (Feb. 1995) and the month preceding the trial (Jan. 1995), which served as the control period. Table II shows the chip analysis for both periods.

AQ was added continuously at the suction of the digester makeup liquor pump at a rate of 0.05% on o.d. wood (1.1 kg/metric ton pulp). The digester additive (Pulp Aid 2M) was injected in the white-liquor line at a rate of 0.05% on o.d. pulp during the last eight days of the one-month trial.

During the first ten days in February, the digester kappa-number target was reduced by 6.8 units (from

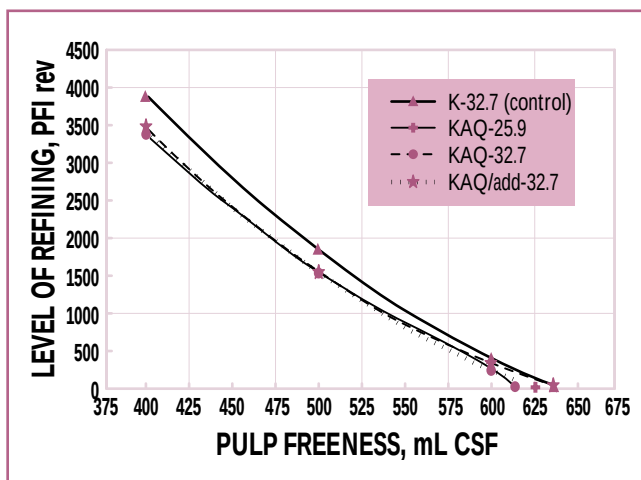
32.7 to 25.9) with AQ addition. For the next ten days, the target was raised to 32.7 with AQ addition only. For the last eight days, the target kappa no. 32.7 was maintained in the presence of both AQ and the digester additive.

The control pulp—a conventional kraft pulp with a target kappa number of 32.7—is identified throughout this paper as K-32.7. The kraft–AQ pulps with kappa-number targets of 25.9 and 32.7 are referred to as KAQ-25.9 and KAQ-32.7, respectively. Finally, the kraft–AQ, digester-additive pulp with a target kappa number of 32.7 is identified as KAQ/add-32.7.

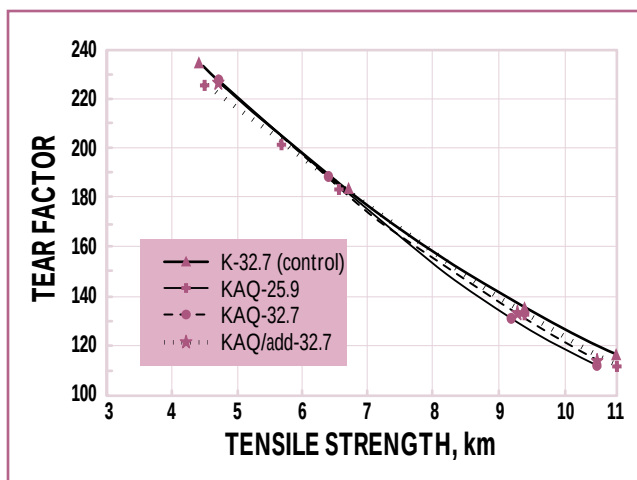
RESULTS AND DISCUSSION

Pulping

Results showing the digester conditions for the control pulp and the three trial pulps are presented in Table III. These data show that pulping to a lower kappa-number target with 0.05% AQ (KAQ-25.9) did not produce a loss in yield when compared with the control pulp (K-32.7). However, solids loading to recovery for the KAQ-25.9 pulp increased approximately 2.5% compared with the KAQ-32.7 pulp. The increase in solids to recovery with no loss in yield for the low-kappa-target pulp (KAQ-25.9) implies that lignin was preferentially dissolved over cellulose. This is also supported



1. Refining energy for control and treated pulps



2. Tear-tensile relationship for control and treated pulps

Bleaching stage	Pulp consistency, % a.d.	Residence time, min	Temp., °C	Tower pH	Substitution, %	ACM*
Chlorination stage	3.5	60	46	...	50	0.16
First extraction stage	10.0	80	74	10.0–10.5	...	...
First dioxide stage	10.0	180	60	3.2–3.8	...	...
Second extraction stage	10.0	90	71	10.5–10.8	...	...
Second dioxide stage	10.0	240	77	3.0–3.5	...	...

*ACM = active chlorine multiple

IV. Bleach-plant operating conditions (held constant throughout control period and trial period)

KEYWORDS

Additives, anthraquinone, bleaching, burst strength, digesters, kappa number, kraft pulping, mechanical properties, pulp properties, tear strength, tensile strength, yield.

by the fact that the hemicellulose content of the KAQ-25.9 pulp was 15.2%, compared with 14.6% for the conventional K-32.7 pulp.

The addition of 0.05% digester additive in combination with 0.05% AQ at target kappa no. 32.7 (KAQ/add-32.7) produced a 1.5-point increase in bleached-pulp yield over the conventional K-32.7 pulp and 0.2-point increase over KAQ-32.7 pulp. The KAQ/add-32.7 pulp also had lower solids loading, digester steam use, and *H*-factor than the K-32.7 or KAQ-32.7 pulps. These results can be ascribed to the fact

that AQ acts as a catalyst to accelerate delignification rate and preserve the hemicellulose, while the digester additive enhances the rate of white-liquor penetration (8). The result is reduced alkali charge, *H*-factor, and lower cook temperature at constant kappa number. The lower temperature when pulping with AQ results in milder cooking conditions and higher pulp yield.

In general, the pulping results show that the KAQ-25.9 pulp had the highest *H*-factors, while the cook temperature and the alkali charge remained essentially the same. The KAQ/add-32.7 pulp showed an improvement in the digester operation as well as pulp yield.

Bleaching

The bleach-plant operating conditions are presented in Table IV. Bleach-plant conditions were held constant throughout the trial period and during the control period.

Table V shows the bleach-plant chemical charges.

Neither the KAQ nor the KAQ/add pulps showed any negative effect on pulp bleachability under the conditions studied. The results in Table V show that the chemical demand in the bleach plant was lowest for the KAQ-25.9 pulp. Chemical demand per unit kappa number for the KAQ-25.9 pulp averaged 4.5% lower than for the conventional K-32.7pulp. The low chemical demand can be explained by the lower organic loading to the bleach plant for the KAQ-25.9 pulp. Moreover, the KAQ-25.9 pulp was also brighter, further reducing the chemical demand. The total oxidizing-power (TOP) demand per kappa-number unit at target kappa nos. 25.9 and 32.7 was 3.50 and 3.66, respectively.

Extending the cook to a lower kappa number reduced the discharge of treated AOX by about 0.6 kg/met-

Condition	CONTROL PERIOD	TRIAL PERIOD (FEB. 1995)		
	(Jan. 1995) K-32.7	2/2–2/10 KAQ-25.9	2/11–2/20 KAQ-32.7	2/21–2/26 KAQ/add-32.7 ^a
Kappa number (blow line)				
Target	32.7	25.9	32.7	32.7
Actual	31.8	26.7	31.4	31.8
Unbleached (decker) pulp	28.4	24.9	28.8	29.2
Production, a.d. metric tons/day	758	803	828	808
Chlorination stage (T-10)				
ClO ₂ , %	0.75	0.73	0.82	0.86
Cl ₂ , %	1.97	1.29	2.06	2.03
TECl ₂ ^b , kg/metric ton	39.4	32.1	42.2	42.9
Active chlorine multiple	0.16	0.14	0.16	0.16
Substitution, %	50	63	53	53
First extraction stage (T-20)				
H ₂ O ₂ , %	0.77	0.68	0.65	0.65
O ₂ , %	0.8	0.8	0.8	0.8
NaOH, %	4.5	2.8	3.4	3.8
NaOH/TECl ₂ ^b (T-10), %	1.14	0.88	0.80	0.88
Target pH	10.5–10.8	10.0–10.5	10.0–10.5	10.0–10.5
First dioxide stage (T-30)				
ClO ₂ , %	1.20	1.00	1.32	1.21
NaOH, %	0.30	0.34	0.37	0.38
Second dioxide stage (T-50)				
ClO ₂ , %	0.34	0.25	0.26	0.25
TECl ₂ ^b , kg/metric ton	79.9	65.0	83.8	81.7
TOP ^c , kg/metric ton	104.0	87.2	105.4	103.3
Brightness, % ISO				
Unbleached (decker) pulp	23.8	26.2	...	...
First dioxide stage exit	81.9	82.8	82.2	82.7
Second dioxide stage exit	89.4	90.0	90.0	90.4
AOX ^d , kg/metric ton	2.0	1.1	1.7	1.5
Pulp viscosity, cP				
Unbleached (decker) pulp	35.1	27.9	33.5	33.5
First extraction stage exit	28.2	21.0	25.2	25.0
Dry end	22.6	19.4	21.1	20.9
Pulp machine				
Headbox freeness, mL CSF	690	...	...	671
Shives, %	0–1	0–3	0–2	0–1
Dirt area, mm ²	0.2–0.6	0.1–1.2	0.2–1.2	0.2–0.7
Dirt count, count/ft ²	1–5	1–5	1–4	1–2
Brightness, % ISO	90.2	89.9	89.9	90.2

^a Digester additive was Pulp Aid 2M, 0.05% on o.d. pulp

^b TECl₂=total equivalent chlorine, which includes Cl₂ and ClO₂

^c TOP=total oxidizing power, which includes Cl₂ and ClO₂, H₂O₂, and O₂

^d Combined treated effluent from Mills A and B

V. Bleach-plant summary before and during the mill trials

ric ton—from an average 1.7 kg/metric ton to 1.1 kg/metric ton—well below British Columbia's 1996 discharge limit of 1.5 kg/metric ton. Decreasing the target kappa number also reduced the consumption of chlorine dioxide, allowing the substi-

tution rate to be raised by 10 points, from 53% to 63%.

Physical properties of finished pulp

Pulps produced under the different conditions were compared by measuring tear factor, burst factor, and

tensile strength. The physical properties of the machine-dried bleached pulps are summarized in Table VI and illustrated in Figs. 1 and 2.

Figure 1 shows that the kraft-AQ pulps required about 13–17% fewer PFI revolutions to achieve the same freeness compared with conven-

Condition	CONTROL PERIOD (Jan. 1995) K-32.7				TRIAL PERIOD (Feb. 1995)											
					2/2-2/10 KAQ-25.9				2/11-2/20 KAQ-32.7				2/21-2/26 KAQ/add-32.7 ^a			
Kappa no. target (blow line) <i>n</i> ^b	32.7 8				25.9 6				32.7 5				32.7 5			
Freeness, mL CSF	637	600	500	400	614	600	500	400	626	600	500	400	636	600	500	400
Refining, PFI rev	0	388	1838	3914	0	240	1533	3383	0	230	1540	3400	0	325	1540	3480
Burst factor	30	49	71	81	33	45	71	82	33	46	71	83	34	50	70	80
Tear factor	234	183	135	116	226	202	133	112	228	188	131	112	227	182	133	114
Tensile strength, km	4.4	6.7	9.4	10.8	4.5	5.7	9.4	10.8	4.7	6.4	9.2	10.5	4.7	6.6	9.3	10.5
Bulk, cm ³ /g	1.85	1.68	1.52	1.45	1.88	1.78	1.54	1.46	1.86	1.75	1.56	1.48	1.81	1.67	1.53	1.45
Porosity, s/100 mL	3.4	7.5	23.3	59.0	3.8	15.8	21.5	54.8	4.0	14.4	19.0	49.6	4.5	9.3	27.2	61.6
Opacity, %	74.1	71.8	67.4	64.9	74.7	73.3	67.7	65.3	74.2	72.8	68.0	66.0	73.6	71.3	67.0	64.8
TEA ^c , J/m ²	48.4	90.0	129.8	146.3	52.6	75.7	127.8	144.7	50.8	81.6	128.4	149.8	54.6	87.5	128.6	145.2

^a Digester additive was Pulp Aid 2M, 0.05% on o.d. pulp
^b *n* = number of tests
^c Tensile energy absorption

VI. Pulp quality before and during the mill trials

tional kraft pulp. The low level of refining can be attributed to the fact that the kraft-AQ pulps have a higher hemicellulose content, as seen in Table III. It is generally accepted that pulps with a high hemicellulose content are easier to refine because the outer structure of the cell wall consists of hemicellulose.

Tear is normally compared with tensile to show a relationship between fiber strength and interfiber bonding. Figure 2 is a graph showing the relationship between tear and tensile. The graph shows that there is no discernible difference between the control pulp and the treated pulps.

CONCLUSIONS

Regulations limiting AOX discharges to 1.5 kg/metric ton of pulp prompted Skeena Cellulose Inc. (SCI) to conduct pulping trials with anthraquinone (AQ) and a digester additive that enhances white-liquor penetration into the chips. Kraft-AQ pulps had a higher bleached yield than the conventional kraft pulp. Extended delignification with AQ showed an increase in solids to

recovery with no loss in yield, implying that AQ selectively removed lignin under prolonged cooking.

Bleaching response of the kraft-AQ pulps was no different than the kraft pulp. As expected, the chemical demand was lowest for the kraft-AQ pulp subjected to extended delignification (KAQ-25.9).

The AOX discharge in the treated effluent decreased by 35% for the kraft-AQ pulp subjected to extended delignification (1.1 kg/metric ton), well below the regulatory limit of 1.5 kg/metric ton in 1996 established by British Columbia.

The pulp treated with AQ and a digester additive had physical properties very similar to the conventional kraft pulp, but these properties were developed with less refining. PFI revolutions to a given freeness were lower by 13–17% for the kraft-AQ pulps compared with the conventional kraft pulp.

The trials demonstrated that SCI can lower the AOX discharge in the treated effluent by using AQ and a digester additive. These additives have additional benefits in the form of lower bleaching costs and wood savings from higher pulp yield. TJ

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