

Paper properties and swelling properties of ozone-based ECF bleached softwood kraft pulps

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ABSTRACT: This study compares the physical properties of DEoQ(PO), (DZ)EoD₁ED₂, and (DZ)EoQ(PO) bleached oxygen delignified softwood kraft pulps to the same properties of a DEoD₁ED₂ bleached ECF reference pulp. Both (DZ)Eo prebleaching and pressurized peroxide final bleaching reduced the AOX formation considerably, although the Q(PO) final bleaching also increased the COD effluent load. The tear strength was maintained, but the (DZ)Eo prebleaching had a slight negative effect on fiber strength as indicated by lower wet zero span strength of beaten (DZ)EoD₁ED₂ and (DZ)EoQ(PO) bleached pulps. Pressurized peroxide final bleaching yielded pulps of higher fiber charge than chlorine dioxide final bleaching. Compared to the D₁ED₂ final bleached pulps, the increased number of charged groups in DEoQ(PO) and (DZ)EoQ(PO) bleached pulps seemed to promote increased fiber swelling of both unbeaten and highly beaten pulps. The more swollen unbeaten Q(PO) final bleached pulps formed denser paper sheets with higher tensile strength and wet zero span strength. A highly charged and swollen pulp seems to be advantageous with respect to beatability when the pulp is beaten to a target tensile strength.

Application: This study shows that correctly applied ozone and hydrogen peroxide can be used to advantage in an ECF bleaching process.

The interest in totally chlorine free (TCF) bleaching chemicals to replace chlorine dioxide accelerated in the 1990s due to both market demand and a desire to further reduce discharges of chlorinated compounds. An important reason for the limited use of TCF chemicals is their low selectivity towards lignin, which causes reduced pulp viscosity and fiber strength [1]. Two recently developed bleaching concepts using ozone and hydrogen peroxide appear to be beneficial from environmental and cost-efficient views relative to traditional elemental chlorine free (ECF) bleaching. The bleaching sequences are termed "ECF light" due to the reduced consumption of chlorine dioxide.

Studies have shown advantages to using ozone in combination with chlorine dioxide in (DZ) and (ZD) prebleaching stages [2,3]. The formation of chloro-organic compounds is reduced and the viscosity of the pulp is maintained when the ozone charge is kept low [2]. In addition, the concept is efficient in terms of delignification and chemical savings. Ozone can be charged both before and after the chlorine dioxide addition in (ZD) and (DZ) stages respectively [4]. Relative to chemical charges, the (DZ) treatment gives the most efficient delignification of oxygen delignified kraft pulp [5]. The (DZ) treatment gave a synergetic delignification effect, with better delignification than expected from the

effect of chlorine dioxide and ozone separately. From a practical point of view, the (DZ) and (ZD) bleaching stages are interesting because the ozone treatment can quite easily be implemented in an existing bleach plant without investing in new, expensive, and space demanding bleaching towers.

Pressurized peroxide bleaching is a possible alternative to chlorine dioxide final bleaching. Pressurized peroxide bleaching (PO)—oxygen pressurized hydrogen peroxide treatment at high temperature—is beneficial in several aspects compared to traditional atmospheric hydrogen peroxide bleaching [6]. The reaction time is reduced considerably, the amount of hydrogen peroxide needed to achieve a target brightness is reduced, the maximum obtainable brightness level is raised, and higher pulp viscosity is obtained [6]. The objective of this study is to compare physical paper properties of various ECF light bleached oxygen delignified softwood kraft pulps to a traditional DEoD₁ED₂ ECF reference pulp. The ECF light bleaching sequences applied were (DZ)EoD₁ED₂, (DZ)EoQ(PO), and DEoQ(PO).

EXPERIMENTAL

These experiments used an industrial oxygen delignified softwood (70:30 mixture of *Picea abies* and *Pinus sylvestris*) kraft pulp of kappa 12.7, brightness 36% ISO and viscosity 930 dm³/kg. After labo-

ratory washing, the pulp was pH adjusted by H₂SO₄ to pH 4, and bleached according to the sequences DEoD₁ED₂, DEoQ(PO), (DZ)EoD₁ED₂, and (DZ)EoQ(PO). The initial D or (DZ) stage was performed at 50°C for 40 min in a high shear medium consistency (MC) mixer. During injection of chemicals, the pulps were fluidized by high intensity mixing. The chemical charges were 0.65% ClO₂ and 0.33% ClO₂ + 0.36% O₃ in the D and (DZ) stages respectively. In the (DZ) stage, ozone was injected after 30 min, when all chlorine dioxide and chlorite should have been consumed. The oxygen reinforced alkali extraction stage, Eo, was performed in autoclaves for 1 h at 90°C, applying 1% NaOH charge and 0.5 MPa oxygen pressure. The batches of DEo and (DZ)Eo prebleached pulps were divided in two portions for D₁ED₂ and Q(PO) final bleaching.

Pulps were acidified by H₂SO₄ to pH 6 prior to the D₁ stage. D₁, E, and D₂ stages were performed in a water bath at 70°C employing retention times of 2 h, 1 h, and 3 h, respectively. Chemical charges were 0.5% ClO₂ in the D₁ stage, 0.4% NaOH in the E stage, and 0.2% ClO₂ in the D₂ stage. Chelation, Q, was done in plastic bags in a water bath for 1 h at pH 5.5 and 70°C, charging 0.3% EDTA. The pressurized peroxide stage (PO) was performed by charging 0.3% MgSO₄, 0.2% DTPA, 1.6% NaOH, and 4.0% H₂O₂, and keeping the pulp in plastic bags within rotating auto-

PULP BLEACHING

	ECF REFERENCE	OZONE ADDED	PEROXIDE ADDED	OZONE + PEROXIDE ADDED
Prebleaching:	DEo	(DZ)Eo	DEo	(DZ)Eo
ClO ₂ , kg Cl/t	3.61	1.84	3.61	1.84
AOX, kg/t	0.32	0.17	0.32	0.17
OCI, kg/t	0.08	0.07	0.08	0.07
Kappa number	3.7	3.1	3.7	3.1
Viscosity, dm ³ /kg	840	730	840	730
Final bleaching:	D ₁ ED ₂	D ₁ ED ₂	Q(PO)	Q(PO)
ClO ₂ , kg Cl/t	3.89	3.89	-	-
AOX, kg/t	0.21	0.23	0.05	0.02
COD, kg/t	8.9	7.7	17.3	18.5
OCI, kg/t	0.08	0.08	0.09	0.03
Viscosity, dm ³ /kg	750	750	770	730
Brightness, % ISO	88.4	87.5	87.5	87.7
Sum ClO ₂ , kg Cl/t	7.5	5.7	3.6	1.8
Sum AOX, kg/t	0.53	0.4	0.37	0.19
Sum COD, kg/t	28.9	26.4	37.3	37.2

1. Characteristics of pulps and effluents.

claves at 105°C, 0.5 MPa oxygen pressure for 2 h. Pulp consistency for all treatments was 10%. Pulps were washed with hot distilled water in between bleaching stages and after the bleaching sequence.

Pulps were analyzed for kappa number (SCAN C 1:77), brightness (SCAN C 11:95), viscosity (SCAN C 15:88), tear strength (SCAN P 11:96), tensile strength (SCAN P 16:76), water retention value (SCAN C-102XE), Scott bond strength, AOX and organic bound chlorine (OCI) in the pulp (SCAN W 9:89). The fiber charge was analyzed by polyelectrolyte adsorption [7] on pulps converted to Na-form [8]. 3.6-ionene (polybrene) with a molecular weight of about 8·10³ g/mole and charge density of 5.12·10⁻³ mole eq/g. was applied without further purification. Hexenuronic acid content was determined by UV spectroscopy [9]. The applied method correlates well with other methods, but somewhat higher values are obtained [10]. Carboxylic acid content in lignin was estimated by analyzing carboxylic acid content in residual lignins by conductometric titration [11] and assuming that total lignin content in the pulps was given by % lignin = 0.15·kappa number. Residual lignins were isolated from the pulps by acidolysis [12].

RESULTS AND DISCUSSION

Bleaching sequences

Table I lists the pulp and effluent characteristics of the final bleached pulps. Chemical charges in final bleaching were chosen to achieve a final brightness target of 88% ISO. Compared to the ECF reference, the total AOX formation was reduced by 25% in the (DZ)EoD₁ED₂ sequence, 30% in the DEoQ(PO) sequence, and 64% in the (DZ)EoQ(PO) sequence. The D₁ED₂ final bleaching accounted for 38% and 58% of the total AOX formation in the DEoD₁ED₂ and (DZ)EoD₁ED₂ sequence, respectively. The (DZ)Eo prebleaching seemed to yield a small reduction in COD effluent load, whereas a substantial increase in dissolution of organic material took place when Q(PO) final bleaching was applied. The dissolution of organic material represents both an increased effluent load and a yield loss. Even though a rather low ozone charge of 0.36% has been applied here, the results in **Table I** show a significant lower viscosity for the (DZ)Eo pre-

bleached pulp compared to the reference pulp. As mentioned, ozone may oxidize polysaccharide chains and form carbonyl and carboxylic structures within the polysaccharide chains. These groups may cause chain cleavage and loss in pulp viscosity upon alkali treatment. However, even though the pulp viscosity of (DZ)Eo prebleached pulps is significantly lower than the DEo prebleached pulp, the results in **Table I** also show that the difference in pulp viscosity decreases considerably after final bleaching.

Physical properties of unbeaten pulps

Table II shows the paper properties of unbeaten pulps. Generally, differences in paper properties were small, and the tear index and fiber-fiber strength (Scott bond) were about equal for all pulps. However, the Q(PO) the final bleached pulps seemed to be somewhat more swollen than the D₁ED₂ final bleached pulps, and somewhat denser paper sheets with higher tensile strength and wet zero span strength were formed.

Laine and Stenius [13] obtained similar results when studying effects of fiber charge on paper properties of industrially bleached kraft pulps. Increased fiber charge promoted increased fiber swelling and flexibility of the fibers. Increased fiber flexibility further promoted fiber conformability and yielded more fiber-fiber contacts. As the fibers remain in contact and form bonds at their intersections upon drying [14] improved fiber flexibility yields denser sheets with higher relative bonded area. The fiber-fiber strength (Scott bond) did not vary much for the pulps investigated. The differences in paper properties of unbeaten pulps in **Table II** can be explained by differences in swelling, consequently, this study further investigated the swelling properties of the pulps.

Effect of bleaching on fiber charge

During kraft cooking a significant number of the initial 4-O-methyl glucuronic acid side groups of xylan is converted to hexenuronic acid groups. Sjöström [15] reported that the content of methyl glucuronic acid groups in *P.abies* and *P.sylvestris* were 70 and 80 µmole/g respectively. Hexenuronic acid is a major contributor to the fiber charge in unbleached kraft pulp, and the variation in fiber charge of ECF and TCF bleached pulps can be largely explained in terms of selective reactions of hexenuronic groups with various bleaching chemicals [16,17].

Table III illustrates the development of total amount of charged groups in the pulps, hexenuronic acid groups, and acid groups attached to lignin in the bleaching sequences applied in this study. The results indicate that the hexenuronic acid groups and charged groups attached to the lignin structure respectively account for about 15% and 20% of the total number of charged groups in the unbleached kraft pulp. However, the total number of charged groups determined by polyelectrolyte titration is probably somewhat overestimated. When comparing the polyelectrolyte titration method with conductometric titration [12], polyelectrolyte titration gave about 15-20 µmole/g higher values for the fiber charge for four different chemical pulps of different charge levels. Even though the total number of charged groups may be overestimated, the hexenuronic acid groups and acid groups attached to lignin account for only about 40% of the total number of charged groups in the pulps. Some of the remaining carboxyl groups may be 4-O-methyl glucuronic acid groups, which were not converted to hexenuronic acid groups in the cook.

In agreement with the literature [16, 17], the results in Table III show that chlorine dioxide and ozone reduces the number of charged groups in the pulp, whereas the amount of charged groups in the pulps remain about constant upon hydrogen peroxide and oxygen treatment. At the same degree of delignification, ozone prebleaching yielded somewhat more efficient degradation of hexenuronic acid groups than did chlorine dioxide. Only traces of hexenuronic acid remained in the pulp after chlorine dioxide final bleaching, whereas a significant amount of hexenuronic acid groups remained in pressurized peroxide final bleached pulps. As the variations in the total number of charged groups in the pulps resemble the variations in the hexenuronic acid group content, the total number of charged groups was also significantly higher for the pressurized peroxide final bleached pulps than for the chlorine dioxide final bleached pulps.

Effect of charged groups on swelling

Generally swelling of cellulosic fibers is governed by the swelling of polysaccharides and by the osmotic pressure created within the fibers due to the dissociation of small ions from charged groups. The swelling is restricted by the ability of the fiber wall to resist the swelling pressure. Upon drying, swelling is reduced due to increased interfibrillar bonding termed hornification. Charged groups promote the swelling of rewetted fibers both by increasing the osmotic pressure and by reducing the degree of hornification upon drying [18, 14]. According to Salmén and Berthold [19], ionic changes mainly affect the surface water of the fibers.

Table IV shows the swelling properties of the various ECF bleached pulps. Q(PO) final bleached pulps are slightly more swollen than the D₁ED₂ final bleached pulps. Although the differences in water retention value (WRV) in Table IV seem small, they are believed to be significant. The errors in WRV are estimated by the standard deviation between replicates, and the obtained errors correspond well to the average standard deviation between replicates reported in the method (SCAN C 62:00). The positive effect of charged groups on swelling is illustrated by the difference in

	DEoD ₁ ED ₂	(DZ)EoD ₁ ED ₂	DEoQ(PO)	(DZ)EoQ(PO)
Tear index, mNm ² /g	20.5 ± 0.7	20.7 ± 0.8	20.7 ± 0.8	20.7 ± 0.7
Tensile index, Nm/g	25.9 ± 0.9	25.2 ± 1.1	26.8 ± 1.1	27.8 ± 1.2
Density, kg/m ³	606 ± 9	609 ± 8	619 ± 9	623 ± 10
Wet zero span, Nm/g	93 ± 5	92 ± 4	98 ± 5	93 ± 4
Scott Bond, J/m ²	100 ± 12	109 ± 10	109 ± 12	109 ± 10
WRV, g/g	1.14	1.17	1.22	1.21
Viscosity, dm ³ /kg	750	790	770	730

Errors are estimated by the standard deviation of replicates

II. Paper properties of unbeaten ECF bleached kraft pulps.

PULP	FIBER CHARGE, μMOLE/g	HEXENURONIC ACID, μMOLE/g	CARBOXYLIC GROUPS IN LIGNIN, μMOLE/g
Unbleached	123	16.9	25
O	113	17.8	20
O DEo	86	9.7	7
O (DZ)Eo	74	7.9	-
O ZEo	76	6.7	10
O DEo D ₁ ED ₂	51	0.3	-
O (DZ)Eo D ₁ ED ₂	49	0.3	-
O DEo Q(PO)	73	10.3	-
O (DZ)Eo Q(PO)	68	7	-

III. Effect of bleaching on charged groups in kraft pulps.

	DEoD ₁ ED ₂	(DZ)EoD ₁ ED ₂	DEoQ(PO)	(DZ)EoQ(PO)
Fiber charge, μmole/g	51	49	73	68
WRV, g/g ¹⁾	1.14 ± 0.01	1.17 ± 0.01	1.22 ± 0.01	1.21 ± 0.01
WRV-WRV _{NaCl} g/g ²⁾	0.01	0.02	0.04	0.06
Na-content, ppm ³⁾	153	140	137	198

¹⁾ Rewetted sheets, ²⁾ WRV in water - WRV in 0.1 M NaCl, ³⁾ 100 ppm Na = 4.4 μmole Na/g

IV. Effect of fiber charge on fiber swelling.

water retention value of fibers in water respective to salt solution, WRV-WRV_{0.1M NaCl}. According to the Donnan Theory [20], salt addition will reduce the difference in total ion concentration between the cell wall and external medium, and reduce the osmotic swelling pressure created by the charged groups. The results in Table IV indicate that the improved swelling of the Q(PO) final bleached pulps can be related to the higher number of charged groups present in these pulps.

Lindström and Carlsson [18] have shown that the ionic form affects the fiber swelling. The degree of hornification was lower for pulps that were dried with acidic groups in ionized form (e.g. in the presence of Na⁺) as compared to pulps with acidic groups in protonized form. In the bleaching sequences applied, the final bleaching stages were both acidic and alkaline, but the pulps were washed with distilled water and pH adjusted to pH 5-6 with SO₂-water after final bleaching. Thus, both chlorine dioxide final bleached pulps and pressurized peroxide final bleached pulps were dried in their protonized form.

Laine and Stenius [14] studied the swelling properties of bleached softwood pulps dried in ionized Na-form and found that the water retention value of rewetted sheets increased by about 0.005 units per charge unit. The results in Table IV indicate that carboxyl groups in the pulps promote swelling even when presented in their protonized form.

Physical properties of beaten pulps

Table V compares the physical properties of beaten pulps. The tear index at tensile index 70 kNm/kg of the (DZ)EoD₁ED₂ bleached and the DEoQ(PO) bleached pulps was about equal to that of the ECF reference. However, the wet zero span strength of beaten pulps was about 8% lower for the pulps in which the (DZ) treatment had been applied. Thus, the (DZ) stage seems to have a slightly negative effect on the fiber strength.

The effect of charged groups on swelling, expressed by WRV-WRV_{NaCl}, seemed to increase at a high degree of beating. Accordingly, Salmén and Berthold [19] observed that the increase in swelling when changing ionic form

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	DEoD ₁ ED ₂	(DZ)EoD ₁ ED ₂	DEoQ(PO)	(DZ)EoQ(PO)
Wet zero span, Nm/g ¹⁾	112 ± 6	103 ± 5	112 ± 5	103 ± 6
Tear index, mNm ² /g ¹⁾	13.4 ± 0.8	14.1 ± 0.9	13.7 ± 0.8	12.3 ± 0.9
Density, kg/m ³ ¹⁾	775 ± 8	762 ± 9	770 ± 9	782 ± 9
PFI mill rev. ¹⁾	3400 ± 200	3000 ± 200	2600 ± 200	3000 ± 200
Scott Bond, J/m ² ²⁾	330 ± 30	300 ± 40	310 ± 30	280 ± 30
Gürley, µm/Pas ¹⁾	16	13	9	6
Light scatt., m ² /kg ¹⁾	20.7	20.8	20.8	20.8
WRV-WRVNaCl, g/g ³⁾	0.06	0.03	0.09	0.09
Shopper Riegler, mL ³⁾	26.5	26.5	29	29

¹⁾ At tensile strength 70 Nm/g, ²⁾ At sheet density 750 kg/m³, ³⁾ At 4000 PFI rev.
Errors are estimated from regression curves of paper properties versus beating degree.

V. Effect of beating on paper properties.

from proton form to sodium form was substantially higher for highly beaten pulps. The reason for this may be that the fibrillated material created in beating have less restricting forces to the osmotic pressure created by the charged groups compared to the unbeaten fiber wall.

As mentioned previously, increased swelling promotes increased fiber flexibility and a sheet of higher tensile strength. Since charged groups promote an increase in swelling for both unbeaten and highly beaten pulps, pulps containing a large number of charged groups should be advantageous with respect to beatability when beating to a target tensile strength. A drawback might be too great an increase in drainage resistance. As shown in Table V, the more swollen Q(PO) bleached fibers also were the ones with the highest Shopper Riegler values.

The results in Table II indicated that the unbeaten Q(PO) final bleached pulps were somewhat more swollen due to the higher amount of charged groups present. The results in Table V indicated that the difference in swelling between the Q(PO) and the D₁ED₂ final bleached pulps was further increased by a high degree of beating. Since increased swelling yields increased fiber flexibility and sheets of higher degree of bonding, highly charged and swollen pulps should be advantageous with respect to beatability when beating to a target tensile strength. Table V shows that beatability, meaning the number of PFI mill revolutions required to reach tensile index 70 Nm/g, was better for the DEoQ(PO) pulp than the DEoD₁ED₂ pulp, but equal for the (DZ)EoQ(PO) and (DZ)EoD₁ED₂ pulps.

The differences in beatability may be influenced by fiber curl introduced by

the fibers through mixing at medium consistency in the first bleaching stage [21]. Somewhat curled fibers probably indicate that all pulps required a rather high amount of energy to reach tensile index of 70 Nm/g. To minimize this effect, pulps were only mixed by high intensity during injection of bleaching chemicals. Since the rewetted zero span tensile strength describes both the strength properties of single fibers and the degree of fiber deformation [22], the lower wet zero span values of the (DZ)Eo-prebleached pulp could be related to more curled fibers. However, considering both the low degree of mixing applied and that lower wet zero span values also were obtained after beating, this is not believed to be the case. PFI mill beating is known to straighten curled fibers [23].

CONCLUSIONS

Physical paper properties of DEoQ(PO), (DZ)EoD₁ED₂, and (DZ)EoQ(PO) bleached pulps to 88% ISO brightness were compared to the same properties of a DEoD₁ED₂ bleached ECF reference pulp.

(DZ)Eo prebleaching applied in a (DZ)EoD₁ED₂ bleaching sequence reduced the AOX formation by 25% and the COD effluent load by 9%. The tear strength was maintained, but the (DZ)Eo prebleaching seems to have a slight negative effect on fiber strength as indicated by lower wet zero span strength of beaten (DZ)EoD₁ED₂ and (DZ)EoQ(PO) bleached pulps.

Pressurized peroxide final bleaching in a DEoQ(PO) bleaching sequence reduced the AOX formation by 30%, but the COD effluent load was increased by 29%. Q(PO) final bleaching yielded pulps with higher fiber charge than chlorine dioxide final bleaching. Compared to the

D₁ED₂ final bleached pulps, the increased number of charged groups in DEoQ(PO) and (DZ)EoQ(PO) bleached pulps seemed to promote increased fiber swelling of both unbeaten and highly beaten pulps. The more swollen unbeaten Q(PO) final bleached pulps formed denser paper sheets with higher tensile strength and wet zero span strength. A highly charged and swollen pulp seems to be advantageous with respect to beatability when the pulp is beaten to a target tensile strength. **TJ**

ACKNOWLEDGEMENTS

The author wishes to thank Peder Kleppe, Björn Dillner, Sissel Ravnsborg, and Størker Moe for valuable discussions and constructive suggestions. Financial support from Norske Skog, Borregaard Ind., Södra Cell, Peterson Linerboard, and the Research Council of Norway is gratefully acknowledged.

LITERATURE CITED

- Gurnagul, N., Page, D.H., Paice, M.G., *Nordic Pulp Paper Res. J.* 7(3):152(1992).
- Dillner, B., Tibbling, P., "Use of ozone at medium consistency for fully bleached pulp," *Int. Pulp Bleach. Conf.*, Stockholm, 2:59-74 (1991).
- Lachenal, D., Taverdet, M.T., Muguet, M., "Improvement in the ozone bleaching of kraft pulps," *Int. Pulp Bleach. Conf.*, Stockholm, 2:33-43 (1991).
- Chirat, C., Lachenal, D., Angelier, R., Viardin, M.-T., *J. Pulp Paper Sci.* 23(6): J289(1997).
- Toven, K., "Ozone based ECF bleaching of oxygen delignified kraft pulp," Doctoral Thesis 98:00, Department of chemical engineering, Norwegian University of Science and Technology, Trondheim, Norway (2000).
- Dillner, B., Tibbling, P., "TCF bleaching can be carried out in different bleaching systems," *XXV EUCEPA Conf.*, Vienna, Austria, 1:65-83 (1993).
- Hynynen, R., Laine, J., Stenius, P., "Determination of the charge of cellulosic fibers by polyelectrolyte adsorption," *NORDPAP DP1/46*, SCAN Forsk report 702 (1998).
- Wåberg, L., Ödberg, L., Glad-Normark, G., *Nordic Pulp Paper Res. J.* 4(2): 71(1989).

9. Gellerstedt, G., Li, J., *Carbohydr. Res.* 294: 41(1996).
10. Tenkanen, M., Gellerstedt, G., Vuorinen, T., et. al., *J. Pulp Paper Sci.* 25(9): 306(1999).
11. Katz, S., Beatson, R.P., Scallan, A.M., *Svensk Papperstidn.* 87(6): R48(1984).
12. Gellerstedt, G., Pranda, J., Lindfors, E.-L., *J. Wood Chem. Technol.* 14(4): 467(1994).
13. Laine, J., Stenius, P., *Paperi Puu* 79(4): 257(1997).
14. Page, D.H., Tydeman, P.A., Hunt, M., "The behaviour of fiber-to-fiber bonds in sheet under dynamic conditions;" in "Formation and structure of paper," *Trans. of the 2nd Oxford Symp.*, 1:249-263 (1961).
15. Sjöström, E., "Wood Chemistry: fundamentals and applications," 2nd ed., Academic Press, Orlando, Florida, USA (1993).
16. Laine, J., *Paperi Puu* 79(8):551-559 (1997).
17. Büchert, J., Teleman, A., Harjunpää, V., et al., *Tappi J.* 78(11): 125(1995).
18. Lindström, T., Carlsson, G., *Svensk Papperstidn.* 85(15): R146(1982).
19. Salmen, L., Berthold, J., "The swelling ability of pulp fibers" In "Fundamentals of papermaking materials," *Trans. of the 11th Fund. Res. Symp.*, 2:683-701 (1997), Cambridge, England.
20. Bolam, T.R., "The Donnan Equilibria," Bell, London, England (1932).
21. Haukjem, S., Toven, K., "Pressurized peroxide bleaching in MC mixer," PFI report 12/96 (1996).
22. Mohlin, U.-B., Alfredsson, C., *Nordic Pulp Paper Res. J.* 5(4): 172(1990).
23. Page, D.H., Seth, R.S., Jordan, B.D., Barbe, M.C., "Curl, crimps, kinks and micro compressions in pulp fibers—Their origin, measurement and significance in papermaking raw materials," *Trans. of the 8th Fund. Res. Symp.*, 1:183-227 (1985), Oxford, England.

Received: November 16, 2000

Revised: January 3, 2002

Accepted: May 22, 2002

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the February *Solutions! for People, Processes and Paper* magazine (Vol. 86 No. 2)

INSIGHTS FROM THE AUTHORS

This work represents the final part of my Ph. D. work. The major objective of my Ph. D. work was to explore the effects of using ozone in (DZ) and (ZD) bleaching stages in ECF bleaching of oxygen delignified softwood kraft pulp. (DZ) and (ZD) stages in prebleaching are considered one way to reduce the chlorine dioxide consumption in traditional ECF bleaching and to provide a more economical and environmental feasible way of bleaching oxygen delignified kraft pulp. The initial investigation looked at fundamental aspects of using a combination of chlorine dioxide and ozone in prebleaching. Delignification efficiency of various combinations of chlorine dioxide and ozone were investigated, as were the residue lignin structure and inorganic chemistries of the (DZ)Eo and (ZD)Eo prebleaching process. The final part of the study, reported here, compared from an economical and environmental point of view the paper and effluent properties of a traditional ECF bleached pulp with pulps bleached with the proposed bleaching sequence.

The most difficult part of this research was to prepare enough pulp to be representative for the bleaching sequence applied. The (DZ) and (PO) bleaching stages are both tricky to perform in the laboratory. Preliminary trials involved varying conditions to find suitable conditions for both the (DZ) and the (PO) treatment.

This study shows that, when applied correctly, ozone and hydrogen peroxide can be used with advantage in an ECF bleaching process. Both chemicals considerably reduce the AOX effluent load and hydrogen peroxide seems to be advantageous in respect to the pulp swelling properties. In addition, the paper strength properties do not differ significantly from the strength properties of the ECF reference pulp. As the (DZ) and (PO) bleaching technology are quite recently developed bleaching concepts, there are only a few similar studies on paper properties reported in the literature. TCF

chemicals, and ozone in particular, have been considered to be detrimental with respect to paper strength, but this study indicates that when the chemicals are applied correctly the paper properties do not have to be affected.

The most interesting finding from this study was that the differences in paper properties could be related to the swelling properties of the pulps. Although the swelling properties were not originally included as part of the research, the differences in paper properties was hard to explain intuitively, and so the swelling properties were studied in more detail.

From a practical point of view, the (DZ) and (ZD) bleaching stages are interesting because the ozone treatment can be easily implemented in an existing bleach plant without investing in new, expensive and space demanding bleaching towers. If, for example, a mill has problems in reaching the brightness target or if the AOX effluent load is too high, this process could be the solution.

The next step for the ozone treatment is to implement the process in the mills, even though a few mills already have done so. A drawback is the rather high investment costs of the ozone plant, so marked demands and/or stricter environmental regulations for discharge of chloro-organic compounds will probably be the driving force for mills to adopt the technology. As hydrogen peroxide seems to be favorable with respect to the swelling properties of the pulp, further research could be to investigate which paper qualities benefit from highly swollen pulps.

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