Upgrading OCC and recycled liner pulps by medium-consistency ozone treatment

MIGUEL ZANUTTINI, THOMAS MCDONOUGH, CHARLES COURCHENE, AND PAULINA MOCCHIUTTI

ABSTRACT: This study evaluated the application of low levels of ozone at medium consistency to improve the properties of old corrugated container (OCC) pulp. Pulps obtained from kraft liner and corrugating medium were also tried. Ozone reduces the kappa number of the pulp, but the surface charge of the fiber is not changed. Ozonation clearly increases the relative bonded area (RBA) in sheets made from treated fibers. It was shown that RBA is essential for Concora medium test (CMT) resistance. Papermaking properties like tensile strength, internal bond strength, compression strength, and CMT were significantly increased even at the lowest ozone charge employed. For OCC pulp, it is shown that similar improvements can be reached by refining and alkali treatment. Nevertheless, alkali has a greater effect on pulp freeness and produces a higher charge in the effluents.

Application: Properties such as internal bond strength, compression strength, and CMT of a recycled unbleached pulp can be notably increased by the application of a little ozone.

Many published studies describe the effects of recycling on papermaking properties such as tensile or tear strength. In comparison, there is less information about effects on properties important for containerboard grades. For the production of test liner or corrugating medium papers, the properties of interest are internal bonding strength and those measured by the ring crush test (RCT), the Concora medium test (CMT), and the short span compression test (SSCT). For board grades, internal bonding strength and stiffness have to be considered.

The strength of a recycled pulp can be improved by increasing fiber conformability or specific bonding strength, both of which may have been affected by the drying operation or by paper end use. Loss of fiber flexibility and inactivation of the fiber surface have previously been shown to result in losses of recycled fiber bonding potential [1].

Refining is the simplest way to recover bonding potential. It has been shown that OCC pulp refining at medium or high consistency gives better results than the corresponding low-consistency operation [2, 3]. In either case, however, the loss in pulp freeness limits the extension of the process [4].

Alkali treatment has been repeatedly analyzed as a means of improving the properties of recycled pulp [5–7]. Zu-Xin Chen and coworkers [7] studied the combination of alkali treatment and refining, and clearly showed that 3% alkali could significantly improve RCT and CMT of OCC. Other authors, however, have shown that alkali may have no effect when chemical pulps are treated under conditions that clearly enhance the properties of mechanical pulps [6]. It is significant that, in spite of the claimed benefits, alkali treatment has not been adopted in industrial recycling processes.

Abadie-Maumert and Soteland [8] and Whitsitt [9] studied the application of high charges of ozone to recycled pulp. Even earlier (in 1973), Procter found that the application of 1% ozone to unrefined, unbleached virgin pulp could increase tensile and burst strengths by 50% without appreciable changes in freeness [10]. In 1985, Abadie-Maumert and Soteland showed that the tensile strength of a recycled packaging paper can be increased by almost 20% by applying 1% ozone [8]. In both studies, the authors did not remove metal ions from the pulp before treatment and they allowed the pH to go from neutral to acidic during ozonation. The use of an acidic pH and control of metal ions are presently considered essential for optimal ozone treatment results.

Because of its high reaction rates with fiber wall components, ozone produces topo-chemical effects [11, 12]. For this reason, it can be expected that oxidation and delignification of fiber surfaces and fines will improve bonding capacity. If so, beneficial effects can be expected even at low levels of ozone application, provided that proper conditions are used. Low levels of fines generation and freeness reduction may also be expected.

In this study, we analyzed the application of low levels of ozone at medium consistency to improve the properties of old corrugated container (OCC) pulp. We separately investigated the corresponding effects on the components of OCC: kraft liner and corrugating medium. We also analyzed the effects of ozonation on bonding potential of the recycled fibers from linerboard. For the OCC pulp, the effects of ozone were compared with those of alkali treatment and refining, known alternatives for improving recycled pulp strength.

EXPERIMENTAL

Materials

Starting materials for the study were the following industrial papers:

- sized kraft liner
- sized corrugating medium paper made from virgin green liquor semichemical pulp, and
- industrial paper made from OCC.

The pulps were prepared by soaking the paper overnight and repulping in a Lamort 25 L pulper. They were acid treated (45 min, pH 2.0) and washed with deionized water to pH 4.0 by diluting and dewatering. Pulps were later centrifuged, shredded, and kept in cold storage until used.

The OCC length weighted (LW) average fiber length determined by an automatic optical analyzer was 1.644 mm.

Ozone treatment

Ozone was applied at medium consistency (15% for liner pulp and 10% for OCC and medium pulp). The pH was adjusted to 3.0 with sulfuric acid. Samples of 300 g of pulp were treated in a CMS 2000 high-shear mixer reactor (CRS Reactor Engineering AB, Sweden) at room temperature. This reactor allows the fast addition of the pressurized ozone-oxygen charge under high-shear mixing conditions. The charge was 0.2%, 0.4%, or 0.8% ozone on pulp. Stirring was immediately stopped when ozone addition was complete. In all cases the applied ozone was completely consumed. Pulp was washed to pH 4.0 with deionized water by diluting to 4% consistency and filtering in a funnel. Pulp was later centrifuged, and kept in cold storage until used.

Other treatments

Samples of OCC pulp were alkali treated at 60°C, and 3% consistency using 1.0% and 2.0% NaOH, based on the o.d. pulp weight. Pulps were washed with deionized water by diluting and filtering. To retain fines, the filtrates were collected and passed again through the fiber mat. Then, the pH was adjusted to 4.0 using sulfuric acid. Pulps were centrifuged, and kept in cold storage until used. Samples of OCC pulp were also refined in a PFI mill at standard conditions. Treatments of 300 and 700 revolutions were applied. The pulp was converted to the calcium form before refining.

Surface charge determination

To determine the surface acid group content of the fibers (R30 fraction), the adsorption isotherms of a high charge density, high molecular weight polyelectrolyte (pDMDAAC, polydimethyldiallylammonium chloride) were used. In general, we followed the procedure applied by Wågberg, et al. [13]. For the colloidal titration, a spectrophotometer equipped with a flow-through cell was used to detect the endpoint by the reduction in the adsorption at 628 nm. The values of each isotherm were fitted to an equation previously proposed [14]. The parameter "Mm" of this equation (the amount of polyelectrolyte stoichiometrically adsorbed) is related to the surface charge values and "r" is related to the affinity between polymer and fiber.

Handsheet preparation

To compare physical properties, all the pulps should be under the same ionic situation. With this aim, not only original but also ozone-treated and alkali-treated pulps, all of them stored at pH 4.0, were converted to the calcium form. We added a solution of calcium hydroxide (20% more than the stoichiometric amount) to the pulp, and later adjusted the pH to 6.0 by adding sodium hydroxide solution. The PFI refined pulp was already in the calcium form. Handsheets of 130 g/m^2 were prepared according to the TAPPI standard procedure.

Determination of bonding capacity of liner pulp fibers

The R30 Bauer McNett fraction of the liner pulp was acid washed and converted to the calcium form. Handsheets of 60 and 130 g/m^2 were prepared according to the standard procedure, with the exception that the pressing pressure was varied from 0.1 MPa to 10 MPa in geometric increments.

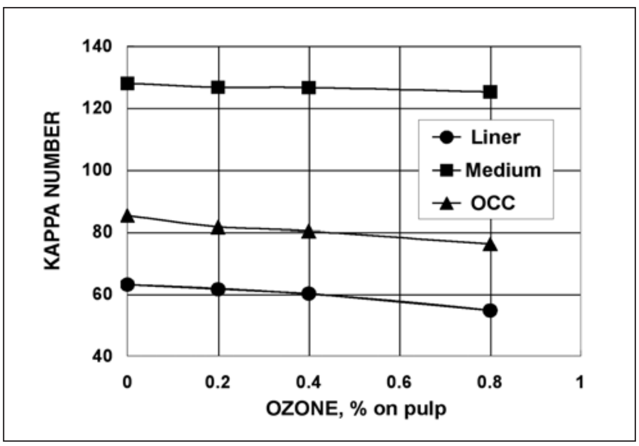
Light scattering coefficient at 681 nm and tensile strength were determined on 60 g/m^2 handsheets. Zero-span tensile strength was determined according to TAPPI T 231 cm-96 Zero-Span Breaking Strength of Pulp using the Clark attachment. Values of CMT and RCT were determined on 130 g/m^2 handsheets.

Curl indices were determined on 5000 fibers of the whole pulp by the fiber quality analyzer (FQA, OpTest Equipment Inc).

RESULTS

Chemical effects

Figure 1 shows that ozonation reduces the kappa number of all three pulps. The kappa of the liner pulp was reduced by 13.2%, from 63.1 to 54.7, but the kappa number of the



1. Kappa number as a function of ozone charge for pulps recycled from kraft liner, semichemical corrugating medium papers, and OCC.

	Mm µeq/g	r µeq/g	R^2
Original pulp	16.2 ± 0,4	125 ± 40	0.984
Pulp treated with 0.8 % ozone	16.4 ± 0,3	239 ± 74	0.992

I. Effect of ozonation of kraft liner fibers on surface properties: Stoichiometric adsorption of pDMDAAC (Mm, related to surface charge) and affinity between polyelectrolyte and surface (r) according to a proposed adsorption equation [14]. The correlation coefficient is indicated.

medium pulp was reduced by only 2% (from 127.9 to 125.2). It may be speculated that the kappa number reduction in the case of the kraft liner pulp is at least partly due to hexenuronic acid removal. The medium pulp is likely to be deficient in hexenuronic acid groups, by virtue of the lower alkalinity of the pulping process used to make it.

Table I shows that ozone application does not produce a detectable increase in the surface acid group content of the liner pulp. Ozone oxidation probably creates acid groups on lignin but, at the same time, hexenuronic acid groups, which are particularly sensitive to ozone treatment, are probably removed.

Ozone effects on bonding capacity of recycled liner pulp

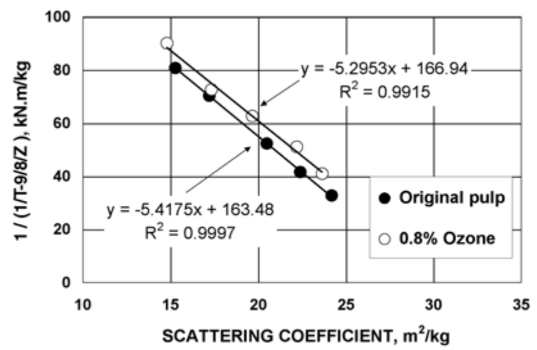
To explore the changes in bonding capacity that ozone treatment can produce, we made use of the Page tensile strength model [15]. Handsheets (60 g/m²) of the R30 fraction of the liner pulp were prepared under different pressing pressures. The Page equation can be written in the form [16]:

$$\left[\frac{1}{T} - \frac{9}{8Z}\right]^{-1} = \frac{b}{k} - \left[\frac{b}{kS_o}\right]S \qquad (1)$$

Where: $k = \dfrac{12c}{PL}$ and $RBA = \dfrac{S_o - S}{S_o}$

T : Tensile index
Z : Zero-span tensile index
c : Fiber coarseness
b : Shear bond strength per unit of bonded surface
P : Fiber perimeter
L : Fiber length
S : Light scattering coefficient
S_o Light scattering coefficient of the unbonded sheet.

Gurnagul and Page [16], emphasized that the model can be applied only if both curl index and zero-span tensile index



2. Page bonding strength index as a function of scattering coefficient. Five pressing pressure were considered.

	ZSTI (Nm/g)	Weighted Curl Index (*)
Original pulp	133	0.071
0.8 % ozone treated pulp	137	0.070

(*) determined by automatic optical analyzer.

II. Zero-span tensile index (ZSTI) and fiber curl index of liner pulp.

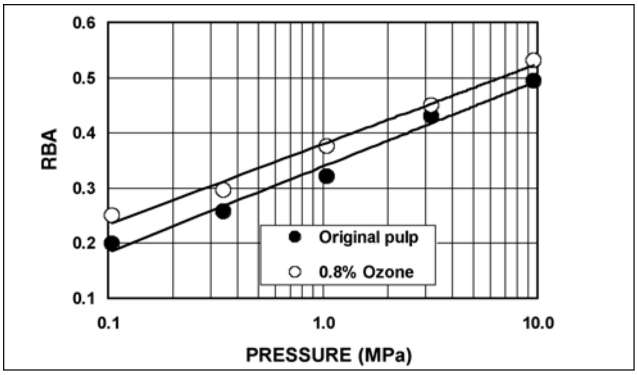
	y-value (b/k)	slope -(b/k) / So	S_o
Original pulp	163.5	- 5.42	30.2
0.8 % ozone treated pulp	166.9	- 5.30	31.5

III. Y-intercepts and slopes of the bonding strength plot (Fig. 2). S_o value is the calculated light scattering coefficient corresponding to the unbonded area.

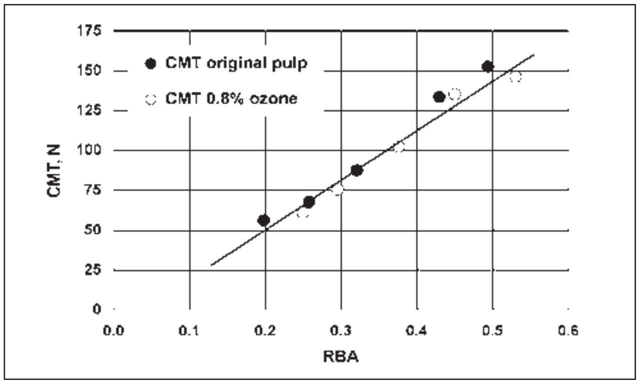
are constant. **Table II** shows that for the original and 0.8% ozone treated pulps these values are similar. **Figure 2** shows the Page bonding strength index (as the left hand side of equation (1) has been called) as a function of scattering coefficient for the original and 0.8% ozone treated pulps. Five pressing pressures were applied. An excellent fit of the experimental values to the equation (1) can be observed.

The b/k and S_o values obtained from Fig. 2, are shown in **Table III**. The values of b/k for the original and ozone treated pulps were similar, which indicates that the specific bond strength was not significantly changed by ozonation.

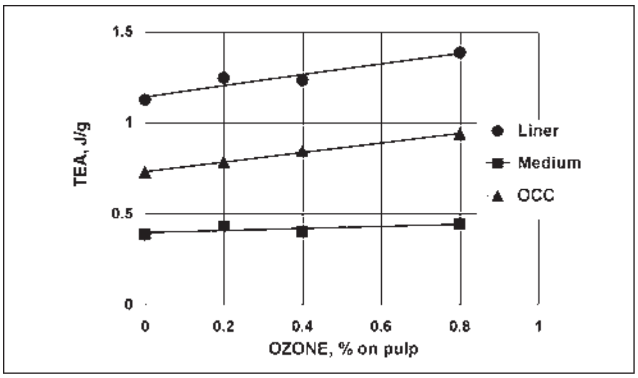
Figure 3 shows that the relative bonded area (RBA) of ozone treated pulp fiber results higher (13% in average) in comparison with original pulp fiber. This result indicates that ozonation produced an increase in fiber conformability.



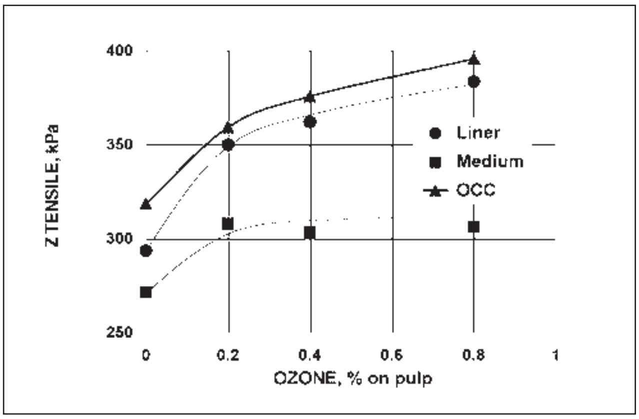
3. Relative bonded area estimated by Page model as a function of the pressing pressure.



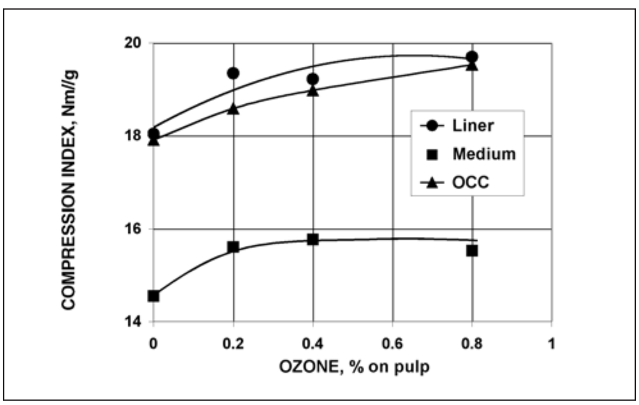
4. CMT value (130 g/m^2 handsheets) as a function of relative bonded area of the R30 fraction of the recycled pulp from liner paper.



5. Tensile energy absorption vs. ozone charge (% on dry pulp).



6. Z direction tensile strength vs. ozone charge.



7. Short span compressive strength (SSCT) vs. ozone charge

Relationship between bonded area and CMT-value for kraft liner fibers

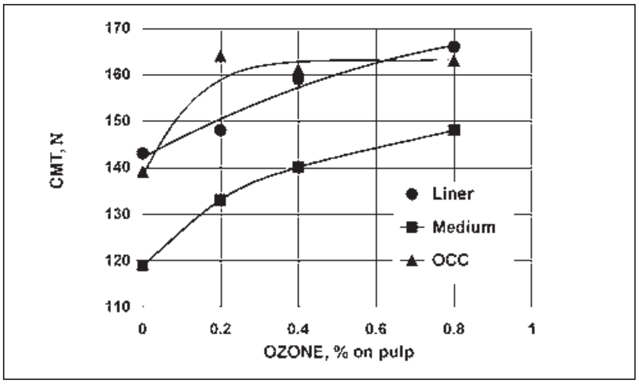
Crush resistances, such as those determined by the flat crush test and RCT of softwood kraft pulps can be increased by increasing pressing pressure [17]. This suggests that the relative bonded area is a determinant of these properties.

Figure 4 shows the CMT value as a function of RBA for 130 g/m^2 handsheets of the liner fibers prepared under the five pressing pressures previously used (Figs. 2 and 3). The same linear relationship, which passes near the origin of the plot, can be observed for both the original and ozone treated pulps, confirming that RBA can be a determinant of the CMT strength. Considering the failure mechanisms in compression described by Feller [18], we can assume that, for these relatively low density sheets, the buckling of the fiber segment in the paper structure generates the fracture process in compression. The increase in RBA implies a reduction in the length of unbonded fiber segments, which can be the reason for the close relationship found here between the RBA and CMT.

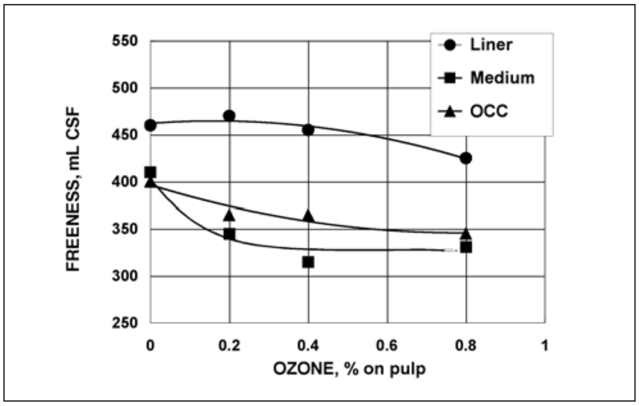
Papermaking properties of pulps obtained from OCC, liner, and medium

Figures 5–8 show tensile energy absorption (TEA), internal bond strength, short span compression resistance and CMT of the three pulps as a function of the ozone charge. Tensile strength of all three pulps is linearly increased by ozonation. TEA is also linearly increased. Figure 5 shows that the TEA of liner and OCC pulps increased by 25% when 0.8% ozone is applied.

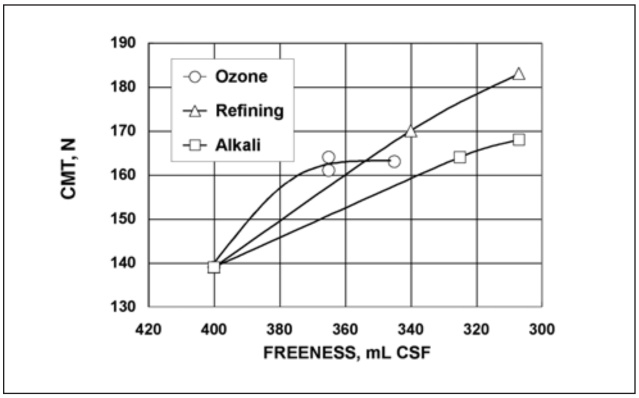
Figure 6 shows that bonding capacity is clearly increased even at low ozone charge. For the three pulps con-



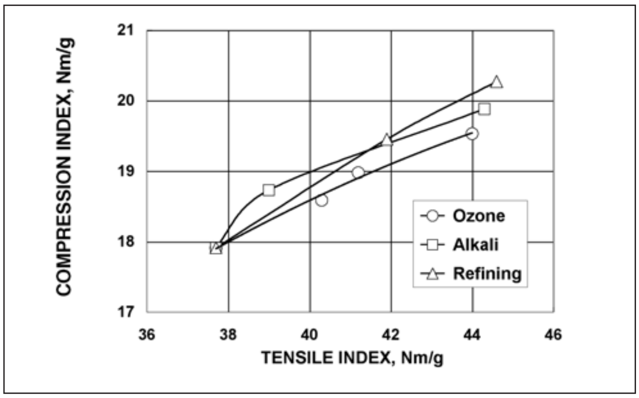
8. Concora crush resistance vs. ozone charge.



9. Freeness vs. ozone charge.



10. Concora crush value against freeness for the three treatments of the OCC pulp.



11. Comparison between the effects of ozone treatment (0.2, 0.4, and 0.8 % on pulp), alkali treatment (1.0 and 2.0 % NaOH on pulp) and refining on compressive and tensile strength of OCC pulp.

sidered, z-direction tensile strength was increased by 30% when the highest charge of ozone was applied. The bonding capacity of the pulp is essential for compression properties according to Fellers [19]. It can therefore be expected that properties like compression strength (SSCT) and Concora crush value (CMT) of these pulps will be improved if bonding capacity is improved. In fact, the SSCT value is increased by 9% for OCC and liner pulps and approximately 18% for the fluting pulp (**Fig. 7**). CMT value is increased by 16% and 25% respectively (**Fig. 8**).

The pulp freeness is negatively affected by ozonation. For OCC pulp, **Fig. 9** shows a reduction in 60 ml CSF. This is in contrast to the low freeness loss observed in previous studies [8, 9].

Comparison between ozonation, refining, and alkali treatment

Figure 10 shows CMT value as a function of freeness. Ozone treatment has the same CMT-freeness relationship as refining, but refining gives a higher level of CMT. Alkali treatment produces a higher detrimental effect on freeness in comparison to both ozone treatment and refining.

Figure 11 shows SSCT value vs. tensile strength of OCC pulp after treatment with 0.2%, 0.4%, and 0.8% ozone on pulp, as well as after alkali treatment with 1.0% and 2% sodium hydroxide and after PFI refining (400 and 700 revolutions). Tensile and compression strengths are improved by the treatments, but ozone appears to have the smallest beneficial effect on compressive strength.

Table IV shows the chemical oxygen demand (COD) produced from the OCC pulp by ozonation and alkali treatment on the treatment liquor and wash water. The release of organic material is clearly lower for the ozone treatment, a difference that represents a clear advantage for the industrial application.

CONCLUSIONS

Medium consistency ozone treatment of the lignified pulps considered here produces a reduction in kappa number, which is proportional to ozone charge. For kraft fibers, it was found that surface charge is not changed. The improvement in bonding capacity that ozonation produced is a consequence of the increase in bonded area. Increasing pressing pressure results in a linear relationship between CMT value and relative bonded area, confirming the importance of bonded areas as a determinant of this

Treatment (% on pulp)	0.4 % O_3	0.8 % O_3	1% NaOH	2% NaOH
COD (% on pulp)	0.26	0.63	1.74	2.77

IV. Total chemical oxygen demand of the processes for the OCC pulp (treatment and washing liquors are considered)

strength property.

Ozone application significantly increases properties of interest for containerboard grades, i.e. internal bonding strength, SSCT, RCT, and CMT. In contrast to previous reports, freeness is negatively affected. For the OCC pulp, we found that similar improvement can be obtained by refining and alkali treatment. Nevertheless, alkali has a greater negative effect on pulp freeness and produces a higher organic load in the effluents.

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INSIGHTS FROM THE AUTHORS


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Refining and alkali treatment are specific means of improving the strength of recycled pulps. Nevertheless, both options affect pulp freeness and, particularly, alkali treatment has not been adopted in industrial recycling processes in spite of the claimed benefits.

Ozone treatment produces oxidation and delignification of high kappa number pulps. An improvement in bonding capacity is produced even at low levels of ozone application, provided that proper conditions are used.

As a contribution to the relatively low knowledge about fundamentals of compression resistance properties, we show here the strong relationship that exists between bonded area of fibers in the sheet structure and the CMT resistance.

We show that the application of low level of ozone at medium pulp consistency significantly increases the properties of interest for containerboard grades. A similar upgrading can be obtained by refining and alkali treatment. Nevertheless, alkali affects more pulp freeness and produces a higher organic load on the effluents.

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