CELLULOSE CHEMISTRY AND TECHNONLOGY

ALKALINE PEROXIDE TREATMENT FOR IMPROVING THE PAPERMAKING PROPERTIES OF RECYCLED UNBLEACHED SOFTWOOD KRAFT PULPS

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The main shortcoming of the papermaking properties of recycled fibres refers mainly to the hornification effect, as a consequence of drying during papermaking. An alkaline treatment is potentially useful to reverse this effect. The present paper discusses the consequences of alkaline and alkaline peroxide treatments on unbleached recycled softwood kraft pulp (Kappa number: 92). A 3^2 factorial experimental design was applied, on considering the following factors: a) total alkaline charge and b) total peroxide charge. The chemical oxygen demand values were used for evaluating the material loss. It was found out that the delignifying effect of alkali was enhanced by peroxide addition. The alkaline treatment reduced freeness and improved the papermaking properties, such as tensile strength, Concora crush strength and short column compressive strength. Also, the addition of peroxide increased the papermaking properties even more, while the material loss caused a considerable increase in the organic charge of the effluents.

Keywords: unbleached pulp, recycling, liner, corrugating medium, COD, CMT, SCT

INTRODUCTION

The ratio of recycled paper used for the worldwide production of paper and boards is continuously increasing[1] (from 38% in 1996 to 53.5% in 2006), as mainly due to the societal and legal requirements now in force.

Recovered unbleached fibres are used for the production of corrugating medium and liner papers, and cardboards. The latter ones are obtained from a mixture of paper, recovered to a different extent which, in addition to unbleached fibres, includes newsprint and magazine papers containing mainly mechanical pulp fibres.

For the production of liner and corrugating papers, old corrugated containers (OCC) represent the main raw material to be recycled. In addition, sack paper (bags of flour, sugar and the like) can be used, however, this type of recovered paper is relatively expensive and has a limited availability. In corrugated board, the most important contribution to weight comes from the liner paper, which contains unbleached kraft long fibres. On the other hand, a fractionation by screen is possible, to obtain – industrially – a stream rich in long fibres. These two reasons show that any alternative for softwood kraft pulp enhancement may potentially improve the quality of the recycled packaging material.

The effects of recycling on brown pulps have not been so extensively studied as those on white pulps. More specifically, in the case of brown kraft pulp, the high content of lignin (10 to 15%), as well as its higher content of hemicellulose, which can be of up to 13.0%, can bring about a singular behaviour.

It has been shown that the loss in wet-flexibility and the inactivation of the fibre surface produces a loss in the bonding capacity of the recycled fibres.[2] Refining is the simplest way for improving the bonding capacity. Nevertheless, the loss in freeness restricts the extension of OCC pulp refining.[3]

Studies on the effects of the alkali treatment of recycled fibres produced different results.[4-6] While Chen *et al.*[6]

obtained improvements in the papermaking properties of different pulps using low alkaline charges, Gurnagul[5] showed that high alkaline charges are necessary for improving the physical properties of the chemical pulps. Disagreements could be due to the fact that the alkali produces a favorable effect on swelling, concomitantly with a negative effect on the hemicellulose loss. Although the benefits of the alkali treatment are widely claimed, it has not been applied yet in industrial processes.

The present work analyzes the effects of an alkali and alkali-peroxide treatment on the papermaking properties of a recycled unbleached softwood kraft pulp (Kappa number: 92). The alkaline treatment – known as potentially useful to reverse the hornification effect – is here applied at a high temperature, with or without the manifestation of any oxidative and delignifying effect of the peroxide. A factorial experimental design is applied, based on the total alkali and total peroxide charge. The chemical oxygen demand, the Kappa number and the papermaking properties – such as tensile index, corrugating medium test (CMT) and short span compression test (SCT) – are also analyzed.

EXPERIMENTAL

Starting material

Treatments were made on a pulp previously subjected to two drying cycles, the former corresponding to the industrial production of liner paper and the latter being obtained in the laboratory. The starting material, industrial liner paper supplied by Papel Misionero S. A. (Argentina), was produced from virgin unbleached softwood kraft pulp (Kappa number: 91.6). It was soaked in the laboratory for 15 h, repulped in a standard laboratory disintegrator (freeness: 715 mL CSF) and then refined in a PFI mill at 4000 revolutions, using a 1.8 N/mm refining load (final freeness: 625 mL CSF). The tensile strength of this pulp (referred to as "original pulp") was of 55.0 kNm/kg.

Sixty 470 g/m^2 handsheets were prepared according to the SCAN-C 26:76 standard procedure. After drying under standard conditions (23 °C; 50% rh), they were oven-dried at 105 °C for 1.5 h, then numbered and stored until use. The handsheets were randomly selected, soaked for 15 h and repulped (referred to as "initial pulp"). The final freeness was of 675 mL CSF and tensile strength was of 30.0 kNm/kg.

Treatments

For favouring the delignifying action of the peroxide, the treatment time adopted (20 min) was sufficient to consume the peroxide charge. The factors selected for the 3^2 experimental design were: alkali charge (0.0, 2.0 and 4.0% sodium hydroxide on o.d. pulp) and hydrogen peroxide charge (0.0, 0.75 and 1.5% hydrogen peroxide on o.d. pulp). The treatments were performed in the presence of a chelator agent (DPTA, Aldrich 0.15% on o.d. pulp) at 70 °C and 10% pulp consistency. The center of the design (3% sodium hydroxide and 0.75% hydrogen peroxide on o.d. pulp) was made by triplicate. In addition, high alkalinity was also applied (6% sodium hydroxide and 1.5% hydrogen peroxide on o.d. pulp). The residual hydrogen peroxide concentration was determined by iodine titration and residual alkali concentration – by acid-base titration.

The treatments were carried out in polyethylene bags, on 20 g of o.d. pulp, at 10% pulp consistency. Reagents were added in the following order: water, alkali solutions, chelator and hydrogen peroxide. Although the hydrogen peroxide partially neutralizes the alkalinity, the initial pH of the treatments was always higher than 13.0.

To rapidly reach the working temperature, the pulp, already placed in the bag, was preheated up to 55 °C in a microwave oven. The pH was again controlled and the bag was placed in a thermostated bath at 70 °C. After 20 min, the liquor sample was immediately extracted for determining the final pH, as well as the residual concentration of alkali and hydrogen peroxide.

Further on, the pulp was diluted with 600 mL of water (final consistency: 2.5%) and filtered. The filtrate was recirculated (passed through the pulp mat) to retain the fines. A sample of this filtrate was used for determining the chemical oxygen demand produced by the treatments. The pulp was concentrated by centrifugation up to 30% of its solid contents and stored at 4 °C.

Handsheet preparation

The pulp was diluted in 1.0 L of water and neutralized with 0.1 N hydrochloric acid up to a pH between 6.5 and 7.5. After 20 min, the pulp was washed and the filtrate was recirculated in each step, until the conductivity in the liquid medium was below 300 μS. The final freeness was determined and 120 g/m^2 handsheets were prepared according to SCAN test methods. The Kappa number and the papermaking properties were determined according to TAPPI test methods.

RESULTS AND DISCUSSION

Table 1 shows that the relative standard errors, induced by the replicates of the central point of the experimental design, were acceptable.

Figure 1 plots the final pH and the residual hydrogen peroxide as a function of alkali charge, as well as the results obtained when high alkalinity and 1.5% hydrogen peroxide on o.d. pulp were used. The final pH increases with the alkaline charge increase, but it is reduced as the percentage of hydrogen peroxide increases. On the other hand, Figure 1 shows that residual peroxide decreases as the alkaline charge increases, which is probably due to the hydrogen peroxide decomposition.

Chemical action: material loss and delignification

Figure 2, illustrating the chemical oxygen demand (expressed as percentage of oxygen on o.d. pulp) as a function of the alkali consumption, shows that, under the experimental conditions applied (20 min, 70 ºC), 50% or more of the alkali charge is not consumed and could be thus recirculated in the process. Alkali consumption appears as a determining factor for the COD produced. When hydrogen peroxide was added, both alkali consumption and the COD increased. The COD reached levels of 6.6% on pulp.

Figure 3 shows the Kappa number as a function of the alkaline charge. The alkaline treatment produces delignification, while hydrogen peroxide produces an additional effect. For 3% NaOH on dried pulp, the peroxide reduced the Kappa number from 75 to 67.

Effects on papermaking properties

Figure 4 plots the tensile index as a function of the alkaline charge. The strength of the original pulp notably decreased due to laboratory papermaking and 105 ºC drying. This detrimental effect can be mostly ascribed to hornification effects. Alkaline treatments partially or totally reverted these effects. The advantages of the alkali (0% hydrogen peroxide) increased moderately by the peroxide action. For 4% sodium hydroxide on pulp, the presence of peroxide increased the tensile index from 47 to 50 kNm/kg.

Table 1
Experimental error calculated from the triplicate of the central point

Response	RSD (%)[*]
Alkali consumption, % NaOH/pulp	3.3
Peroxide consumption, % H_2O_2/pulp	0.8
COD, % O_2/pulp	5.4
Freeness, mL CSF	0.6
Tensile index, kNm/kg	1.2
CMT, N	1.8
SCT, kN/m	1.8

[*] RSD: Relative standard deviation

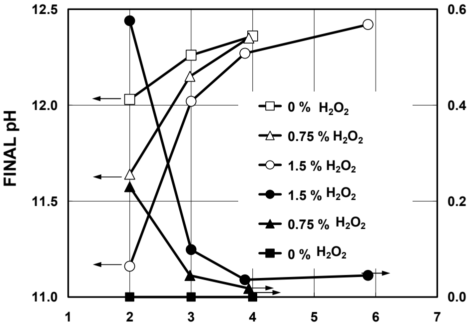

Figure 1: Final pH and residual hydrogen peroxide as a function of alkaline charge (% NaOH/o.d. pulp) for three levels of H_2O_2 (% on o.d. pulp). For 1.5% H_2O_2 on o.d. pulp, an additional experiment of high alkali charge (6% NaOH on o.d. pulp) is included

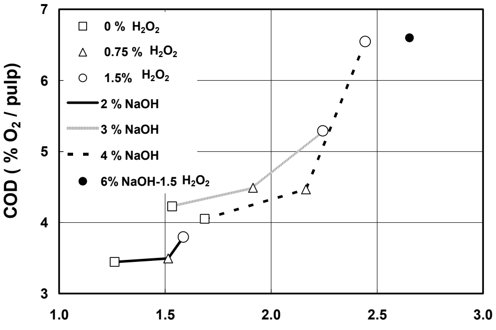

Figure 2: Chemical oxygen demand as a function of alkali consumption during alkali and alkali peroxide treatments. Mostly, there is only one relationship between COD and alkali consumption

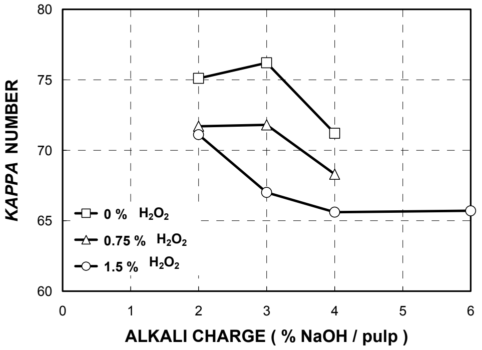

Figure 3: Kappa number as a function of alkali charge. The Kappa number of the original pulp was of 91.6

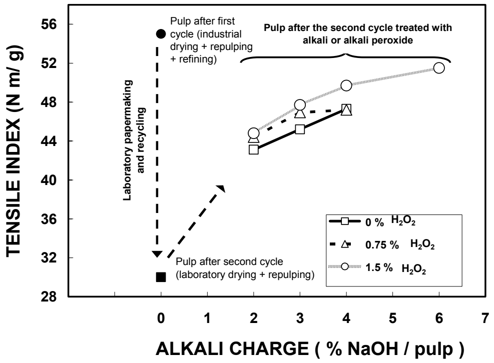

Figure 4: Tensile strength as a function of alkali charge. Three levels of alkali and peroxide charge are considered. The tensile index of the original pulp is reduced from 55.0 Nm/g to 30.0 Nm/g (initial pulp), as due to laboratory recycling

Figure 4 also shows that low alkaline charges are sufficient for enhancing the tensile strength of this pulp, which agrees with the results obtains by Chen *et al.*[6] for old corrugated container pulps (OCC).

Figure 5 shows the CMT values as a function of alkali consumption. The alkaline or alkali-peroxide treatment notably increased the CMT values, similarly with the case of tensile strength. As a result of the treatments, CMT increases from 49 N to 128-170 N. In alkali-peroxide treatments, the presence of peroxide, which increases alkali consumption, increased the CMT value only slightly.

Figure 6 shows the linear relation between the short compression strength and tensile strength, probably due to the fact that both properties strongly depend on the bonding capacity level. The higher the alkali or the alkali peroxide charges, the higher the tensile and the compression strength properties are.

Table 2 lists the results of the fitting second order polynomial equations to the CMT, COD and freeness data, on considering the alkaline charge and peroxide consumption.

The contour plots of these regression equations (Fig. 7) show that the higher the alkaline charge and the peroxide consumption, the higher the CMT results are, while freeness is less affected. The contour plot indicates that the high COD produced by the peroxide makes the increase in alkaline charge more convenient than the increase in the peroxide charge.

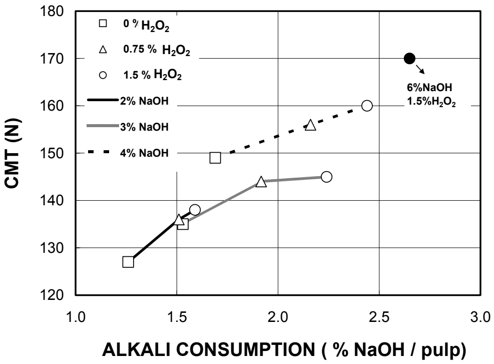

Figure 5: Concora crush resistance as a function of alkali consumption. Three levels of alkali and peroxide charge are considered. The CMT value of the initial pulp was of 49.0 N

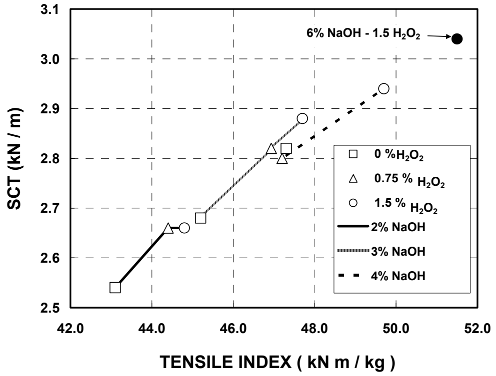

Figure 6: Short compression resistance as a function of tensile strength. Mostly, there is only one relationship between these properties. Three levels of alkali and peroxide charge are considered

Table 2
Results of regression equations fitting the experimental data

Response	Equations		R^2 adjusted
CMT, N	$113.6 + 8.267 \times X + 7.626 \times Y$	[1]	91.9%
Freeness, mL CSF	$670 - 16.68 \times X - 3.482 \times X \times Y + 1.801 \times X^2$	[2]	90.6%
COD, % O_2/pulp	$2.7 + 0.401 \times X + 0.845 \times Y^2$	[3]	89.5%

X: Alkali charge (% NaOH/o.d. pulp); Y: Peroxide consumption (% H_2O_2/o.d. pulp)

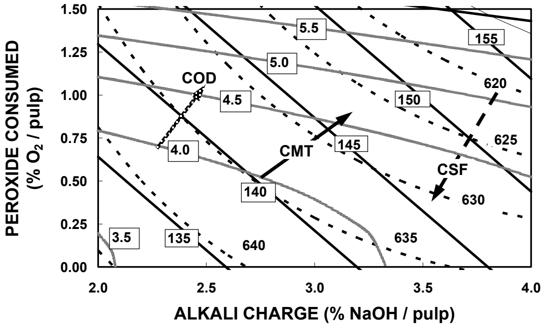

Figure 7: Contour plot of CMT (N), COD (% O_2/o.d. pulp) and freeness (mL CSF) as a function of alkali charge (% NaOH/o.d. pulp) and peroxide consumption (% H_2O_2/o.d. pulp). The CMT and freeness of the initial pulp were of 49.0 N and 675 mL CSF, respectively

CONCLUSIONS

The disadvantage of the papermaking properties of unbleached recycled softwood kraft pulps, induced by drying, were reverted by alkali or alkali-peroxide treatments, even at low alkaline charges.

The alkaline treatment improves pulp strength. The tensile index increased more than by 50%. Under the experimental conditions used (20 min; 70 °C), 50% or more of the alkaline charge was not consumed and could be thus recirculated in the process.

The alkaline-peroxide treatments produced higher delignification and better papermaking properties than the simple alkaline treatment.

As the tensile index and the short span compression test evidence a similar behaviour, it could be said that the improvement in paper strength was due to the improvement in bonding capacity.

The addition of hydrogen peroxide produced only a minor improvement in the papermaking properties. The SCT increased by 5% and the CMT increased by 7%, as compared to the simple alkaline treatment. Nevertheless, the amount of dissolved material was notably increased by peroxide for the highest alkaline charge used (4.0% sodium hydroxide). Peroxide addition produced a 60% increase in the dissolved material, as measured by the oxygen chemical demand.

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