CHARACTERIZATION OF *Eucalyptus grandis* KRAFT PULPS TREATED WITH PHOSPHONATES IN DIFFERENT STAGES OF TCF BLEACHING

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The addition of a phosphonated chelant (DTPMPA) at different points of a TCF bleaching sequence and its effect on pulp properties were studied in this work. An industrial *Eucalyptus grandis* kraft pulp was submitted to a counter-ion exchange (Ca^{2+} or Na^{+} form) and was then bleached using DTPMPA in the washing or in the bleaching stages of two distinct sequences: OOpP and OQOpP (20 pulps). The counter-ion exchange affected fibre length, as well as the handsheets bulk and air permeability (higher for Na^{+}-based pulps) and handsheet tensile strength, brightness, skeletal density, and total porosity based on Hg porosimetry (higher for Ca^{2+}-based pulps). The hydrogen peroxide consumption in Op and P stages achieved the lowest values when the chelant was distributed rather than applied in a separate Q stage. The addition of chelant in the P stage provides pulps with higher ISO brightness (>85%). The chelant effects were always more noticeable in Ca^{2+}-based pulps.

Keywords: Kraft pulp - TCF bleaching – chelating agent – phosphonates – Eucalyptus

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INTRODUCTION

The decline of chlorine-based bleaching reagents (chiefly chlorine) and the increase in the use of oxygen-based chemicals, such as oxygen (O-stage), hydrogen peroxide (P-stage), ozone (Z-stage), and peracetic acid (Pa-stage), are the consequences of many factors. The most important of them are the need to improve the pulp quality (strength properties, cleanliness, whiteness, brightness stability), production flexibility and ease of control, as well as the need to reduce the water consumption (partial or total closure of water circulation), and the amount of dioxins and adsorbable organochlorine compounds (AOX) in both effluents and pulps. The highest usage of oxygen-based chemicals is associated with TCF (Total Chlorine Free) bleaching sequences. However, these reagents are very sensitive to the presence of transition metals that catalyse radicals' formation (Heikkilä and Vuorinen 2000).

For instance, in the P-stage, the unselective nature of radicals' action has a positive effect on brightness but has a negative effect on both polysaccharides depolymerisation and hydrogen peroxide decomposition. Pulp pre-treatment in an acid

stage (A-stage) for metals leaching or in a chelating stage (Q-stage) followed by an effective pulp washing are usually employed (Lapierre et al. 1997). The Q-stage is normally operated under acidic conditions where the chelants commonly used have their maximum chelating power. Being acidic, the corresponding effluents are problematic from the prospective of circuit closure. On the other hand, the phosphonated chelating agent DTPMPA (diethylene triamine penta methylene phosphonic acid) has been shown in our previous works to be effective in reducing metal ions in alkaline medium, and can be added directly into the digester or into the O- or P-stages (Area and Felissia 2005; Felissia and Area 2004). These studies have also revealed that the early removal of metal ions (in the cooking and washing steps) using this chelant improves significantly the TCF bleaching of eucalypt kraft pulps. Moreover, DTPMPA caused an increase in pulp strength properties (Area and Felissia 2005; Area and Felissia 2007; Felissia and Area 2004). The best bleaching sequence obtained was then applied to an industrial pulp with encouraging results (Area and Felissia 2007).

Even if phosphonates could be somewhat more expensive than other chelants, they also have been shown to prevent scale formation (Felissia et al. 2007), decreasing the cost of maintenance, lost production, shutdowns to make repairs of equipment, etc. Phosphonates have a very strong interaction with surfaces, which results in a significant metal removal in technical and natural systems. Due to this strong adsorption, little or no remobilization of metals is expected. As phosphonates are mainly present as Ca and Mg-complexes in natural waters, they do not affect metal speciation or transport (Nowak 2003).

The effects found on the pulp with the application of phosphonates were interpreted in terms of ionic equilibrium in the fibres (Area and Felissia 2007), because DTPMPA caused a 30% decrease in the Ca^{+2} content, whereas Na^{+} content increased. The valence of the counter-ion of the dissociated acid groups in the pulp fibres is known to affect the swelling degree and the capacity of fibre bonding, and therefore the strength of pulp sheets, following the order $Na^{+} > Ca^{+2} > Mg^{+2} > H^{+} > Al^{+3}$ (Scallan and Grignon 1979). Consequently, changing cations from calcium to sodium form of an unbeaten pulp will give the same beneficial effect than a certain amount of beating energy required to attain a certain tensile strength. This is particularly important in the case of industrial pulps, as they are usually in the Ca^{+2} form due to the process waters (Hammar et al. 2000). While one of the main sources of calcium in the system is the wood, it has been demonstrated that in pulps manufactured from the same raw material the calcium content is 5 times lower when they are washed with demineralized water than when they are washed with tap water (Area and Felissia 2007).

Considering these results, a new study was designed to analyse the effect of the counter-ion exchange (Na^{+} and Ca^{+2}) and of DTPMPA addition during cooking and pulp washing on the properties of both industrial and laboratory *Eucalyptus grandis* kraft pulps (Area et al. 2010a). The results have shown that the laboratory brownstock pulp required lower beating energy than the industrial brownstock pulp to achieve 30 ºSR, and the corresponding handsheets exhibited better strength and optical properties, as well as a more homogeneous and smooth surface. A later study demonstrated that there are differences in the bond strength per unit of bonded area of fibers, due to the nature and content of cations in the fibers (Area et al. 2010b). The counter-ion exchange operation

diminished the mechanical strength properties and increased brightness, with the effects of the Ca^{+2} greater than those of Na^{+}. On the other hand, the addition of DTPMPA in the cooking stage decreased the calcium content but did not show a prominent impact on the optical and mechanical properties, and it tended to increase the surface heterogeneity, the specific surface area, and the porosity (Area et al. 2010a).

The objective of the present work was to complete aforementioned investigation in order to evaluate the effect of the phosphonate chelant DTPMPA on the fibre characteristics and on the handsheet properties using pulps in which the change of base was performed (sodium or calcium form). For both calcium-based and sodium-based pulps, DTPMPA was added in the washing and the bleaching stages using the sequences OOpP (oxygen, oxygen reinforced hydrogen peroxide stage, peroxide) and OQOpP (with a separate chelation stage). An industrial pulp of *Eucalyptus grandis* was submitted to a change of base with the counter-ions Na^{+} or Ca^{+2} and then bleached utilizing different chelant addition points. In total, 20 different pulps were obtained. These pulps were characterized with respect to kappa number, viscosity, hexenuronic acid content, crystallinity index, optical and mechanical properties, air permeability, apparent density and true density, total porosity, and specific surface area. The morphological characteristics of the fibres were evaluated by means of an automated image analysis system, and their effects on the remaining pulp properties were also studied.

EXPERIMENTAL

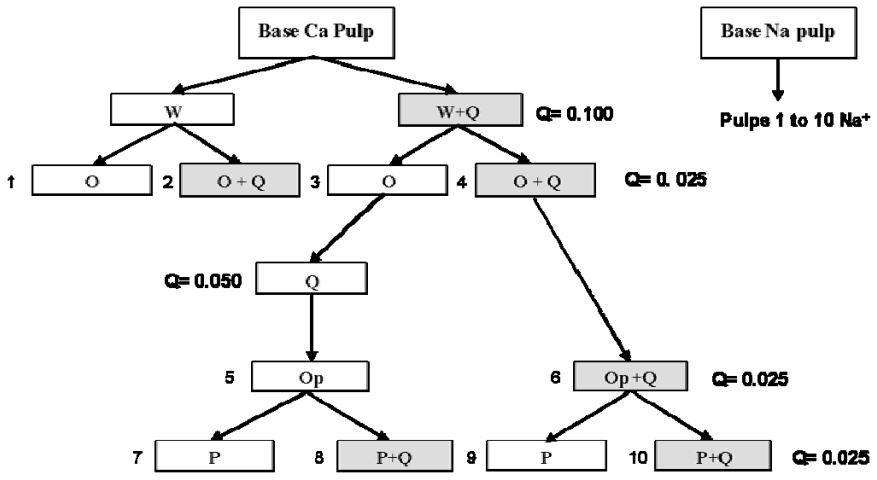
An industrial unbleached kraft pulp of *Eucalyptus grandis* was used with the following metal ion content: 31.2 meq/kg of Ca, 4.80 meq/kg of Na, 4.46 meq/kg of Mg, 0.74 meq/kg of Mn, 0.63 meq/kg of Fe, and 1.44 meq/kg of Cu. The mechanical properties of the corresponding handsheets before and after a counter-ion exchange process were presented in a previous article (Area et al. 2010a) and are listed in the first line of some of the tables that follow.

For the counter-ion exchange process the pulp was firstly protonated with HCl for 2 h, at room temperature. The pulp consistency and the acid concentration were 1% and 0.1M, respectively. The pulp was thereafter washed with demineralized water until a pH of 6 in the filtrate was reached. Then, the pulp was treated with either a 0.1M aqueous solution of $CaCl_2$ or NaCl, for 2 h and with agitation intervals of 20 min at room temperature, in order to obtain the Ca^{2+} or the Na^{+} forms. Finally, each pulp was centrifuged and washed again with demineralized water.

A chelating stage (Q) was performed in one half of the Ca^{2+}- and Na^{+}-based pulps using 0.1% of DTPMPA (as active acid) at pH 9 (Fig. 1). The treatment time was 30 min, with agitation intervals of 10 min. Each pulp was centrifuged until a consistency of 30%. The resulting chelated pulps were subjected to the bleaching sequences OQOpP and OOpP, with or without chelant addition in the O, Op, and P stages, as detailed in Fig. 1. Therefore, 20 pulps were produced: 10 Na-based pulps and 10 Ca-based pulps. Table 1 shows the operating conditions of the different stages.

All the pulps were characterized in terms of kappa number and viscosity, according to the TAPPI standards, and hexenuronic acid content (HexA), according to the

spectrophotometric method reported by Chai et al. (2001), adopted as the official procedure TAPPI T 282, with a time of 80 min (determined *ad-hoc* for these pulps). The metal content in the pulps was determined by atomic absorption spectroscopy with a Perkin Elmer Analyst 200 model. The acidic groups content of pulps was determined by conductimetric titration, according to the procedure described by Lloyd and Horne (1993), and adapted from Katz et al. (1984).



Base Ca or Na pulp	Total quantity of Q
1	0
2	0.025
3	0.100
4	0.125
5	0.150
6	0.150
7	0.150
8	0.175
9	0.150
10	0.175

Figure 1. Experimental design and amount of chelant added (% odp)

Table 1. Operating Conditions of the O, Q, Op, and P Stages(a)

	O	Q DTPMPA	Op	P
Oxygen pressure (kg/cm^2)	6	--	6	--
Consistency (%)	10	3	10	10
Temperature (ºC)	100	60	100	90
Time (min)	30	30	120	120
NaOH charge (% odp)	2.0	--	1.0	1.5
H_2O_2 charge (% odp)	--	--	1	3
$MgSO_4$ charge (% odp)	0.05	--	0.05	0.10
pH of the stage	11.8	9.0	11.0	11.2
(a) - % odp: percent of oven dried pulp				

The pulps were beaten in a PFI mill until around 30 SR (1000 revolutions for Ca-based pulps and 700 revolutions for Na-based pulps, approximately) according to the TAPPI T248cm standard. TAPPI standards were also followed for the characterization of the corresponding handsheets regarding the mechanical properties. As for optical properties and bulk, ISO standards were used. Other handsheet properties were evaluated: true density, by helium picnometry (Accupyc 1330, Micromeritics, Norcross (Atlanta), Georgia, USA); porosity, by mercury intrusion porosimetry (Poresizer 9320, Micromeritics); and specific surface area, by the BET krypton adsorption method (ASAP 2000, Micromeritics). Mercury porosimetry was also used to determine the handsheets'

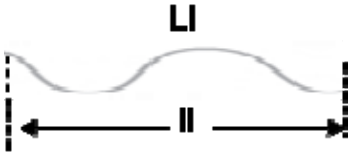
bulk density and skeletal density, defined as the weight per unit volume of sample after subtracting the volume of the pores larger than approximately 200 μm and 0.007 μm, respectively (Moura et al. 2005).

A Philips XPert diffractometer (Almelo, The Netherlands) having a Co radiation source at 40 kW and 35 mA was used to determine the crystallinity index (CI) by X-ray diffraction, defined as follows:

$$CI = \frac{I_c - I_a}{I_c} \times 100 \quad (1)$$

In Eq. (1) I_c and I_a are the intensities of the peaks corresponding to the crystalline (maximum intensity of 002 peak) and to the amorphous (at 2θ=22º) parts of the diffractogram, respectively, as determined with ORIGIN 6.1 software.

Microscopic properties were also determined using a Zeiss trinocular microscope with a computerized image analysis (LEICA QWIN software): the fibre length, *Li*, the projected fibre length in different angles, *li*, the mean fibre length (number weighted), the curl index of each fibre, *CuIi*, the length weighted mean curl index, *CuIw*, as well as the kink index, *KI*. Since the curvature of the fibres is affected by drying, 200 fibres were analyzed in wet pulp samples. The curl Index of each fibre was calculated by Eq. 2 (Trepanier 1998), whereas the length weighted curl index was calculated based on the total measured fibres (Eq.3).



$$CuIi = \frac{Li}{li} - 1 \quad (2)$$

$$CuIw = \frac{\sum CuIi \times Li}{\sum Li} \quad (3)$$

The kink index was computed by Eq. 4 (Trepanier 1998),

$$KI = \frac{1N_{(10º\text{-}20º)} + 2N_{(21º\text{-}45º)} + 3N_{(46º\text{-}90º)} + 4N_{(91º\text{-}180º)}}{\sum Li} \quad (4)$$

where $N_{(\alpha\text{-}\beta)}$ is the number of fibres counted with angles between α and β.

Using the Statgraphics software (StatPoint, Inc., Warrenton, Virginia) the analysis of variance (95% probability level) was performed for each stage of the bleaching sequence. The significant differences and the corresponding p values were reported. The correlation of the response variables was also analyzed.

RESULTS AND DISCUSSION

Oxygen-based reagents, such as oxygen or hydrogen peroxide, are prone to generate radicals, especially in the presence of transition metals. Such radicals contribute not only to the bleaching action but also to an extensive depolymerization of the polysaccharides (Wuorimaa et al. 2006). Moreover, Fe and Mn can also compete with Ca and Na in the exchange of base. However, it is known that an acid treatment at pH 2.5 eliminates most of these ions. In fact, in this study, Fe and Mg were not detected after the base exchange treatment of the pulps.

The results of the chemical analyses of the pulps are presented in Tables 2a and 2b. In both cases, the pulp kappa number decreased significantly ($p = 0.0000$) in each of the stages illustrated in Fig. 1, with greater decreases in the O (Δ Kappa ca. 4) and Op (Δ Kappa ca. 2) stages. The pulp viscosity had a slight decrease in the P stage. However, the biggest drop was observed in the O stage.

Table 2a. Chemical Characteristics of the Ca-based pulps (see Fig. 1) after each Stage (Unb – original unbleached pulp)

Pulps	Kappa number	Viscosity [cP]	Metal content [meq/kg]			HexA [mmol/kg]	Total acidic groups [mmol/kg]	Cl [%]
			Na	Ca	Mg			
Unb.	12.5	27.2	4.8	31.2	4.5	49	65	48
1	8.7	16.1	11.5	34.7	33.2	42	70	58
2	8.7	15.9	31.0	21.9	32.9	45	71	61
3	8.5	15.8	34.4	37.0	38.5	41	69	62
4	8.7	15.9	34.4	32.3	37.0	45	71	-
5	6.4	15.6	19.4	27.8	27.4	48	67	71
6	6.5	15.8	31.1	22.9	42.7	48	67	73
7	6.1	15.2	12.2	22.6	51.6	43	73	-
8	6.1	14.6	11.0	21.0	51.2	45	74	-
9	6.0	15.0	11.5	14.9	56.5	47	70	72
10	6.0	15.5	9.6	14.3	55.6	46	64	84

Table 2b. Chemical Characteristics of the Na-based pulps (see Fig. 1) after each Stage (Unb – original unbleached pulp)

Pulps	Kappa number	Viscosity [cP]	Metal content [meq/kg]			HexA [mmol/kg]	Total acidic groups [mmol/kg]
			Na	Ca	Mg		
Unb.	12.5	27.2	4.8	31.2	4.5	49	65
1	8.5	16.2	50.8	1.3	36.6	42	67
2	8.7	16.1	49.0	0.2	27.9	40	70
3	8.4	16.0	70.7	0.5	42.0	39	66
4	8.7	16.1	68.0	0.5	34.4	47	70
5	6.6	15.9	45.4	1.7	50.9	45	63
6	6.5	15.7	32.5	1.6	66.6	49	67
7	6.1	14.5	12.8	3.8	64.5	36	70
8	6.1	15.0	14.5	2.3	62.1	44	70
9	6.0	15.0	10.7	2.1	69.3	47	67
10	6.1	15.4	9.5	2.2	68.9	46	60

The initial goal of the counter-ion exchange process was to turn the dissociated acid groups into the Na^+ and Ca^{2+} forms. However, the addition of Mg^{2+} (as a stabilizer) in the O, Op, and P stages changed the metal content of the pulps in such a way that after the P stage Mg^{2+} was the most abundant ion. In fact, the initial "calcium-based pulp" possessed a similar amount of Ca^{2+} and Na^+ after the P stage, while the initial "sodium-based pulp" possessed a low amount of Ca^{2+}. The addition of Mg^{2+} also increased the content of Na^+ in the O stage due to the liquor alkalinity.

The hexenuronic acid content after the O, Op, and P stages was slightly lower than in the unbleached pulp. The variations observed are the result of the balance between two opposite factors: 1) the formation in the alkaline medium of new hexenuronic acids from the pulp residual glucuronic acids and 2) the dissolution of hexenuronic acids together with xylose units due to the alkaline degradation of the xylan backbone. The crystallinity index of the Ca-based pulp increases with the extent of the oxidizing treatment, mainly in the O and Op stages, where the delignification is higher. The crystallinity index also increases with the amount of chelant applied.

The physical and mechanical properties after beating are presented in Tables 3a (calcium-based pulps) and 3b (sodium-based pulps).

Table 3a. Physical and Mechanical Properties of the Ca-based Pulps after Beating (Unb – original unbleached pulp)

Ca-based pulps	SR	Bulk [cm^3/g]	Tear index [mN m^2/g]	Tensile index [N m/g]	Air permeability [µm/Pa s]
Unb.	28	1.297	8.1	89.1	3.8
1	28	1.341	6.9	66.1	6.1
2	28	1.345	6.7	69.6	6.0
3	28	1.321	6.8	72.6	4.7
4	28	1.317	6.6	68.7	6.2
5	34	1.294	8.3	72.8	4.6
6	33	1.317	8.6	72.2	4.2
7	34	1.318	8.5	67.2	7.4
8	32	1.303	8.8	69.4	5.5
9	33	1.302	8.4	70.7	5.4
10	32	1.301	7.8	72.3	4.3

Table 3b. Physical and Mechanical Properties of the Na-based Pulps after Beating (Unb – original unbleached pulp)

Na-based pulps	SR	Bulk [cm^3/g]	Tear index [mN m^2/g]	Tensile index [N m/g]	Air permeability [µm/Pa s]
Unb.	28	1.297	8.1	89.1	3.8
1	28	1.395	7.3	63.0	9.3
2	28	1.370	7.4	61.1	7.3
3	28	1.385	6.8	62.7	8.6
4	28	1.378	6.8	63.6	9.3
5	30	1.377	7.9	61.2	8.2
6	30	1.384	8.4	61.8	10.2
7	28	1.365	7.9	60.5	12.7
8	28	1.358	8.5	61.1	9.7
9	28	1.336	8.7	62.1	10.0
10	28	1.382	7.7	59.0	12.0

In general, the bulk and, accordingly, the air permeability, were higher in the sodium-based pulp ($p = 0.0109$ and $p = 0.0000$, respectively), while the tensile index was higher in the calcium-based pulp ($p = 0.0000$). The tear index increased upon applying the Op stage ($p = 0.0000$) and was maintained after the subsequent stages, in accordance with the evolution of the crystallinity index. Similarly to the latter, the tear index increased significantly ($p = 0.0000$) with the amount of chelant applied.

The results of the peroxide consumed in the Op and P bleaching stages, as well as the optical properties, are shown in Table 4. The consumption of peroxide diminished drastically upon incorporating the chelant in the Op ($p = 0.0011$) and P ($p = 0.0002$) stages, but depended on the amount of chelant added ($p = 0.0353$). Therefore, the distribution of the chelant between the Op and O stages is a better option than its addition in a single alkaline Q stage. A negative correlation was found between the consumption of H_2O_2 in the P stage and the HexA content This could be explained by the chelating action of the latter (Devenyns and Chauveheid 1997; Vuorinen et al. 1999) or, alternatively, by the DTPMPA action, avoiding the peroxide decomposition (lower consumption) and the formation of free radicals that produce the xylan degradation and, consequently, the dissolution of the HexA associated with it. A correlation between HexA content and the optical properties was not observed.

Table 4. Hydrogen Peroxide Consumption (Op plus P stages) and Optical Properties of the Ca- and Na-based pulps (Unb. = original unbleached pulp)

Pulp	H_2O_2 consumption (%)		ISO brightness (%)		*L**		*a**		*b**	
	Ca	Na	Ca	Na	Ca	Na	Ca	Na	Ca	Na
Unb.	-	-	30.9		71		5.1		15.7	
1	-	-	50.9	51.6	84	85	2.4	2.5	14.3	13.8
2	-	-	53.2	53.1	85	85	2.4	2.6	13.7	13.8
3	-	-	52.6	52.3	85	85	2.4	2.6	13.8	13.8
4	-	-	53.1	53.4	85	86	2.4	2.6	13.7	13.9
5	89.7	85.9	76.3	73.7	95	94	0.3	0.7	9.0	9.8
6	69.5	74.3	78.3	74.6	95	94	0.4	0.5	8.1	9.6
7	35.7	38.3	83.9	82.5	97	96	0.2	0.3	6.2	6.7
8	28.2	25.9	85.9	82.9	97	96	0.03	0.2	5.5	6.7
9	29.0	30.4	84.3	82.7	97	96	-0.01	0.2	6.3	6.8
10	21.3	22.0	85.4	82.7	97	97	-0.16	0.1	5.5	6.9

In general, brightness increased significantly from O to Op stage (more than 20% ISO) and increased slightly with the P stage (around 8% ISO) ($p = 0.000$). Besides, the brightness gain in O, Op, and P stages, in relation to the kappa number loss, increased in the ratio of about 5:1, 10:1, and 20:1, respectively. The brightness was higher for the calcium-based pulps ($p = 0.0077$) and, mainly for these pulps, increased with the addition of chelant in the peroxide stage ($p = 0.0002$, interaction $p = 0.0191$ for Ca and chelant

factors). Therefore, the highest brightness (over 85% ISO) was obtained in the calcium-based pulps with the addition of chelant in the P stage. The effect on the colour parameter *b** was opposite (less yellow with chelant addition in the P stage, for the calcium based pulps). The significant effect of the interaction ion exchange-chelant addition ($p = 0.0036$) indicates that the parameter *b** was not modified by the chelant addition in the P stage for the sodium-based pulps, but diminished markedly for the calcium-based pulps. The analysis of the parameter *a** indicates that the sodium-based pulps were more reddish ($p = 0.0026$). The presence of chelant in the Op and P stages diminished the reddish tone ($p = 0.0111$ and $p = 0.0281$, respectively) but the variations were always more pronounced in the calcium-based pulps.

Table 5 reports the biometric parameters of the fibres. The mean fibre length was superior in the sodium-based pulps ($p= 0.0018$). However it slightly decreased with the presence of chelant in the P stage ($p= 0.0325$), mainly for the calcium-based pulps. At this level of fibre length, a higher length led to the production of handsheets that were more bulky (*Li* correlates positively with bulk, $p= 0.0087$), with the consequent decrease of the tensile strength ($p= 0.0033$) and increase of the air permeability ($p= 0.0017$).

The mechanical treatment during beating may cause internal tensions in the fibres leading to the formation of curls and kinks that can negatively influence the dry strength properties (Page and Seth 1980; Page et al. 1984; Robertsen and Joutsimo 2005; Trepanier 1998). The values of the weighted curl index (*CuIw*) were higher than other reported values for hardwoods, although the manual measurement resulted in values 20% higher than the automatic ones (Robertson et al. 1999). The kink index (*KI*) was lower for the Na-based pulps ($p= 0.0474$) and decreased with chelant addition in the Op stage ($p= 0.0474$). The significant interaction between both ($p= 0.0132$), indicated that changes of this index did not occur for Na-based pulps, whereas KI deeply decreased with chelant addition in the Op stage for the Ca-based pulps. A correlation between these indexes and the mechanical properties was not observed.

Table 5. Biometric Parameters: Fibres Mean Length, Weighted Curl Index and Kink Index

Pulp	Mean Li [µm]		CuIw		KI	
	Ca	Na	Ca	Na	Ca	Na
7	868	894	0.13	0.13	0.007	0.005
8	825	881	0.11	0.13	0.008	0.005
9	853	890	0.12	0.11	0.005	0.005
10	840	887	0.12	0.12	0.005	0.006

Tables 6a and 6b show other handsheet physical and surface properties. The difference observed between the true density (He picnometry) and the skeletal density (Hg porosimetry) revealed the presence of very small pores (<0.007 µm), which are not counted due to the maximum pressure that can be used in the of mercury intrusion process (Moura el al. 2005). The sodium-based pulps exhibited higher differences between these two properties.

Table 6a. Other Handsheet Physical Properties of the Ca-based pulps (Unb. = original unbleached pulp)

Ca-based pulps	True density (He picnometry) [g/cm^3]	Skeletal density (Hg porosimetry) [g/cm^3]	Bulk density (Hg porosimetry) [g/cm^3]	Apparent density[a] (ISO 534) [g/cm^3]	Total porosity (Hg porosimetry) [%]	Specific surface area [m²/g]
Unb.	1.43	1.47	0.78	0.771	47	0.6
1	1.65	1.17	0.82	0.746	30	0.9
2	1.65	1.14	0.82	0.744	28	0.8
3	1.58	1.17	0.80	0.757	32	0.7
4	1.63	1.18	0.82	0.759	30	0.8
5	1.63	1.32	0.83	0.773	38	0.8
6	1.60	1.21	0.79	0.759	25	0.8
7	1.61	1.42	0.80	0.759	40	0.7
8	1.62	1.45	0.83	0.767	30	0.7
9	1.54	1.28	0.84	0.768	34	0.8
10	1.62	1.23	0.86	0.769	30	0.7

[a] - Inverse of bulk, Table 3a.

Table 6b. Other Handsheet Physical Properties of the Na-based Pulps (Unb. = original unbleached pulp)

Na-based pulps	True density (He picnometry) [g/cm^3]	Skeletal density (Hg porosimetry) [g/cm^3]	Bulk density (Hg porosimetry) [g/cm^3]	Apparent density* (ISO 534) [g/cm^3]	Total porosity (Hg porosimetry) [%]	Specific surface area [m²/g]
Unb.	1.43	1.47	0.78	0.771	47	0.6
1	1.53	1.23	0.77	0.717	32	0.8
2	1.60	0.98	0.77	0.730	21	0.8
3	1.61	1.13	0.77	0.722	32	0.8
4	1.63	1.18	0.77	0.726	29	0.8
5	1.61	1.13	0.79	0.726	30	0.8
6	1.63	1.05	0.79	0.722	24	0.7
7	1.58	1.20	0.79	0.732	34	0.8
8	1.64	1.06	0.79	0.736	25	0.8
9	1.63	1.11	0.78	0.749	30	0.7
10	1.63	0.98	0.77	0.724	26	0.8

* - Inverse of bulk, Table 3b.

The greater variation of the true density was registered in the first oxygen stage, where most of the residual lignin is removed (the initial pulp exhibited a value of 1.43 g/cm^3). The skeletal, bulk density (Hg porosimetry) and apparent density (ISO 534) were lower in the sodium-based pulps ($p= 0.0034$). The first of them was also lower when the chelant was added in the P stage ($p= 0.0439$), and this relationship showed higher

correlations with the remaining properties. It correlated negatively with the bulk (p= 0.0021) and with the air permeability (p= 0.0097) and in a positive way with the carboxylic acids content (0.0131), the tensile index (p= 0.0093), and total porosity (p=0.0118). The simultaneous increase of the skeletal density and of the porosity means that the pores that are relevant for porosity were those of the interfibre spaces instead of those of the fibre wall. The bulk density showed a positive correlation with the apparent density (p= 0.0047), with the tensile index (p= 0.0040), and with the air permeability (p= 0.0043).

Regarding the porosity, a greater variation was also observed in the first oxygen stage due to the greater delignification (the unbleached pulp exhibited a value of 47%). The decrease in the values of this property is in agreement with the observed increase of the true density in the same stage. In general, the total porosity was lower in the Na-based pulps (p= 0.0216) and decreased when the chelant was added in the O (p= 0.001), Op, and P stages. Similarly, the porosity decreased when the total amount of chelant was distributed between the two O stages, instead of being applied in a separate Q-stage. The greater variations in the specific surface were also observed in the O stage (0.6 m^2/g in the unbleached pulp).

CONCLUSIONS

1. This work demonstrates that the *Eucalyptus grandis* kraft pulps considered in this work act as ion exchange agents. Therefore, their properties are strongly affected not only by the wood chemical composition, but also by the counterion, the kind of water of the mill, the various chemical products that are added during the process, and the closure of water circuits. Chelating agent such as DTPMPA, which can be added in any stage in a wide pH range, are capable of modifying the ionic balance in the different stages, thus allowing a certain manipulation of the properties of the pulps.
2. The ion-exchange process (Na or Ca form) influences the mean fibre length and the kinks, as well as the handsheets' bulk, air permeability (higher in the Na-based pulps), tensile index, brightness, skeletal, bulk and apparent density, and also the total porosity based on Hg porosimetry (higher in the Ca-based pulps). Nevertheless, the addition of Mg^{2+} as a stabilizer into the O, Op, and P stages changes the pulp ion content, being the most abundant ion after the P stage. In fact, the pulps initially "Ca-based" exhibited equal amounts of Ca^{2+} and Na^{+} after the P stage, whereas the pulps initially "Na-based" exhibited a very low amount of Ca^{2+}.
3. The addition of more than 0.1% of the chelant DTPMPA increases, in general, the crystallinity index, the amount of hexenuronic acids, and the tear index, and increases air permeability in all sequences. The effects of the chelant were always more pronounced in the Ca-based pulps. The distribution of the chelant between the O and Op stages had a more positive effect than its alternative use in an additional Q-stage in a separated reactor. The introduction of the chelant in the P stage leads to pulps with higher final brightness (> 85% ISO). Under these conditions, the handsheets are less yellow and less reddish and exhibit higher tensile index and lower air

permeability, because the fibrous structure is more closed, although their fibres are shorter (mainly in the Ca-based pulps).

4. In the studied bleaching sequences (OOpP and OQOpP), the O-stage is the one that promotes the greatest delignification by unit of brightness gain, whereas in the P stage the decrease of the kappa number is very low. Besides the brightness and the tear index, the crystallinity index increases continuously throughout the bleaching process, due to the removal of the amorphous material.

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NOMENCLATURE

CI	Crystallinity index
CuIi	Curl index (for each fibre)
CuIw	Weighted Curl index
DTPMPA	Diethylene triamine penta(methylene phosphonic acid)
HexA	Hexenuronic acid
KI	Kink index
Li	Fibre length
li	Projected fibre length
odp	Oven dried pulp
Q	Chelating stage with DTPMPA
O	Oxygen delignification stage
O + Q	Oxygen delignification stage with the addition of DTPMPA
Op	Oxygen delignification stage reinforced with hydrogen peroxide
Op + Q	Oxygen delignification stage reinforced with hydrogen peroxide and the addition of DTPMPA
P	Hydrogen peroxide stage
P + Q	Hydrogen peroxide stage with the addition of DTPMPA
TCF	Total Chlorine Free
W	Washing stage

REFERENCES CITED

Area, M. C., Carvalho, M. G. V. S., Ferreira, P. J., Felissia, F. E., Barboza, O. M., and Bengoechea, D. I. (2010a). "The influence of pulping and washing conditions on the properties of *Eucalyptus grandis* unbleached kraft pulps treated with chelants", *Bioresour. Technol.* 101(6), 1877-1884.

Area, M. C., Benítez, J., and Felissia F. E. (2010b). "Tensile strentgth components of *Eucalyptus grandis* kraft pulps," *O Papel* 71(8), 48-62.

Area, M. C., and Felissia, F. E. (2007). "Bleaching Eucalyptus grandis kraft pulps using a short TCF sequence," *TAPPSA Journal*, March. (http://www.tappsa.co.za/html/statistical_process_control.html).

Area, M. C., and Felissia, F. E. (2005). "Chelating agents management to obtain TCF bleached *Eucalyptus grandis* kraft pulps," *Appita J.* 58(2), 143-148.

Chai, X.-S., Zhu, J. Y., and Li, J. (2001). "A simple and rapid method to determine hexeneuronic acid groups in chemical pulps," *J. Pulp Pap. Sci.* 27(5), 165.

Devenyns, J., and Chauveheid, E. (1997). "Uronic acids and metals control," *Proceedings of 9th Int. Symp. on Wood and Pulping Chemistry*, June 9-12, Montreal, Technical Section CPPA, M5-1-M5-4.

Felissia, F. E., and Area, M. C. (2004). "Phosphonates in kraft pulping and brown stock washing of Eucalyptus pulps," *Appita J.* 57(1), 30-34.

Felissia, F. E., Area, M. C., Barboza, O. M., and Bengoechea, D. I. (2007). "Anti-scaling agents in kraft pulping," *BioResources* 2(2), 252-264.

Hammar, L.-A., Backstrom, M., and Htun, M. (2000). "Effect of the counterion on the beatability of unbleached kraft pulps," *Nord. Pulp Pap. Res. J.* 15(3), 189-193.

Heikkilä, M., and Vuorinen, T. (2000). "Decomposition of hydrogen peroxide in catalytic cycle," *Proceedings of Int. Pulp Bleaching Conf.*, June 27-30, Halifax, Nova Scotia, Canada, 155-160.

Katz, S., Beatson, R. P., and Scallan, A. M. (1984). "Determination of strong and weak acidic groups in sulfite pulps," *Svensk Papperstid.* 87(6), R48-53.

Lapierre, L., Paleologou, M., Berry, R. M., Bouchard, J. (1997). "The limits of metal removal from kraft pulp by acid treatment," *J. Pulp Pap. Sci.* 23(11), J539-J542.

Lloyd, J. A., and Horne, C. W. (1993). "The determination of fibre charge and acidic groups of radiata pine pulps," *Nord. Pulp Pap. Res. J.* 1, 48-52 and 67.

Moura, M. J., Ferreira, P. J., and Figueiredo, M. M. (2005). "Mercury intrusion porosimetry - A valuable tool for the characterization of wood, pulp and paper," *Powder Technol.* 160(2), 61-66.

Nowack, B (2003). "Environmental chemistry of phosphonates," *Water Research* 37(11), 2533-2546.

Page, D. H., Barbie, M. C., Seth, R. S., and Jordan, B. D. (1984). "The mechanism of curl creation, removal and retention in pulp fibres," *J. Pulp Pap. Sci.* 10(3), 574-579.

Page, D. H., and Seth, R. S. (1980). "The elastic modulus of paper III. The effect of dislocations, microcompressions, curl and kinks," *Tappi J.* 63(10), 99-102.

Robertsen, L., and Joutsimo, O. (2005). "The effect of mechanical treatment on kraft pulps produced from different softwood raw materials," *Pap. Puu*. 87, 111-115.

Robertson, G., Olson, J., Allen, P., Chan, B., and Seth, J. (1999). "Measurement of fibre length, coarseness, and shape with the fibre quality analyser," *Tappi J.* 82(10), 93-98.

Scallan, A. M., and Grignon, J. (1979). "The effect of cations on pulp and paper properties," *Svensk Papperstidn*. 82(2), 40-47.

Trepanier, R. I. (1998). "Automatic fiber length and shape measurement by image analysis," *Tappi J*. 81(6), 152-154.

Vuorinen, T., Fagerström, P., Buchert, J., Tenkanen, M., and Teleman, A. (1999). "Selective hydrolysis of hexenuronic acid groups and its aplication in ECF and TCF bleaching of kraft pulps," *J. Pulp Pap. Sci*. 25(5), 155-162.

Wuorimaa, A., Jokela, R., and Aksela, R. (2006). "Recent developments in the stabilization of hydrogen peroxide bleaching of pulps: An overview," *Nord. Pulp Paper Res. J.* 21, 435-443.

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