Chelating agents management to obtain TCF bleached *Eucalyptus grandis* kraft pulps

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Summary

This work studies phosphonates performance when added in laboratory kraft *Eucalyptus grandis* TCF bleaching (O-Q-Op-P). The experimental design (16 final pulps) included sequences of brown stock washed with DTPMPA, a control using a classical EDTA Q stage, EDTA and DTPMPA combinations, and Q stage elimination. Results show that Mn and Fe content in pulps are not statistically different when applying a Q stage with the same quantity of EDTA or DTPMPA. Metals removal is more efficient when chelant load is distributed between stages than when applied only in a Q stage. Chelant incorporation in O stage washing water noticeably improves pulp brightness. The best choice includes DTPMPA in brown stock washing, elimination of the Q stage, DTPMPA in the Op stage, and DTPMPA in the P stage. Optimising the P stage of this sequence can result in 50% peroxide residual, which can be recycled to the Op stage.

Keywords

Kraft pulps, TCF bleaching, chelating agents, phosphonates, *Eucalyptus grandis*

Water consumption minimisation, waste reduction, and capital investment optimisation are some of the keys of minimum-impact manufacturing (*1*). Although ECF or TCF bleaching effluent elimination is not necessary for environmental protection, there is a lot to do regarding process economy and profit maximisation.

In peroxide bleaching, hydroxyl radicals (HO•), which are extremely reactive and indiscriminate (attacking cellulose as well as lignin), are generated by peroxide decomposition; the reaction is catalysed by metallic ions present in the pulp (*2*). Controlling organic peroxides formation and reaction will promote better pulp brightness and physical properties. Since wood itself contains Mn^{+2}, Fe^{+3} and Cu^{+2}, metal management in an early stage of pulp production or handling could be advantageous. The development of methods to control organic peroxides formation before or during the O stage is therefore extremely valuable.

EDTA (ethylene diamine tetra acetic acid), the most popular chelating agent in the pulp and paper industry, requires acidic conditions. An acidic stage involves sulfuric acid addition, and supplementary equipment and manipulation costs, including special materials of construction. Alternatively, phosphonates, which function in strong alkaline medium, proved recently to be very effective in metal management (*3-5*).

This work studies different strategies of chelant application in a simple eucalypt kraft totally chlorine free (TCF) bleaching process (O-Q-Op-P).

DTPMPA (diethylene triamine penta(methylene phosphonic acid)) is applied in cooking, washing and TCF bleaching stages (all in alkaline media), and their performance is compared with EDTA in acid media.

DTPMPA incorporation is recommended in stages where significant improvements are achieved.

EXPERIMENTAL

Materials

Eucalypt (95% *grandis*) chips from Celulosa Argentina, Capitán Bermúdez mill was the raw material used. Chips were classified with a square mesh, retaining the fraction between 25mm and 5mm. Evident knots and bark were hand rejected.

Solutia Inc. provided the phosphonates (Dequest 2066).

Total experimental design

Figure 1 shows the experimental sequence of the whole study. The design was established on the basis of results of a previous study (*3*), including sequences of brown stock washed with DTPMPA. In the control line, (1-19 series) the only chelant application is a conventional EDTA Q stage. Other sequences combine EDTA and DTPMPA, and elimination of the Q stage.

As this design is a typical hierarchical or nested plan, evaluation of the results used Variance Components Analysis. The experiment design nested pulps tested into peroxide stages, into washing stages, and into Op stages.

Table 1 presents total chelant charge in the studied sequences.

Table 1
Total application of chelants in pulps (identified by numbers in Fig. 1).

Experiment no.	EDTA	DTPMPA odp* % a.a.b.** (cumulative)	DTPMPA kg product/t (cumulative)
19	0.125	–	–
20	0.125	0.025	1
21	0.125	0.025	1
22	0.125	0.050	2
23	–	0.125	5
24	–	0.150	6
25	–	0.150	6
26	–	0.175	7
27	–	0.125	5
28	–	0.150	6
29	–	0.150	6
30	–	0.175	7
31	–	0.125	5
32	–	0.150	6
33	–	0.150	6
34	–	0.175	7

* o.d. pulp
** active acid basis

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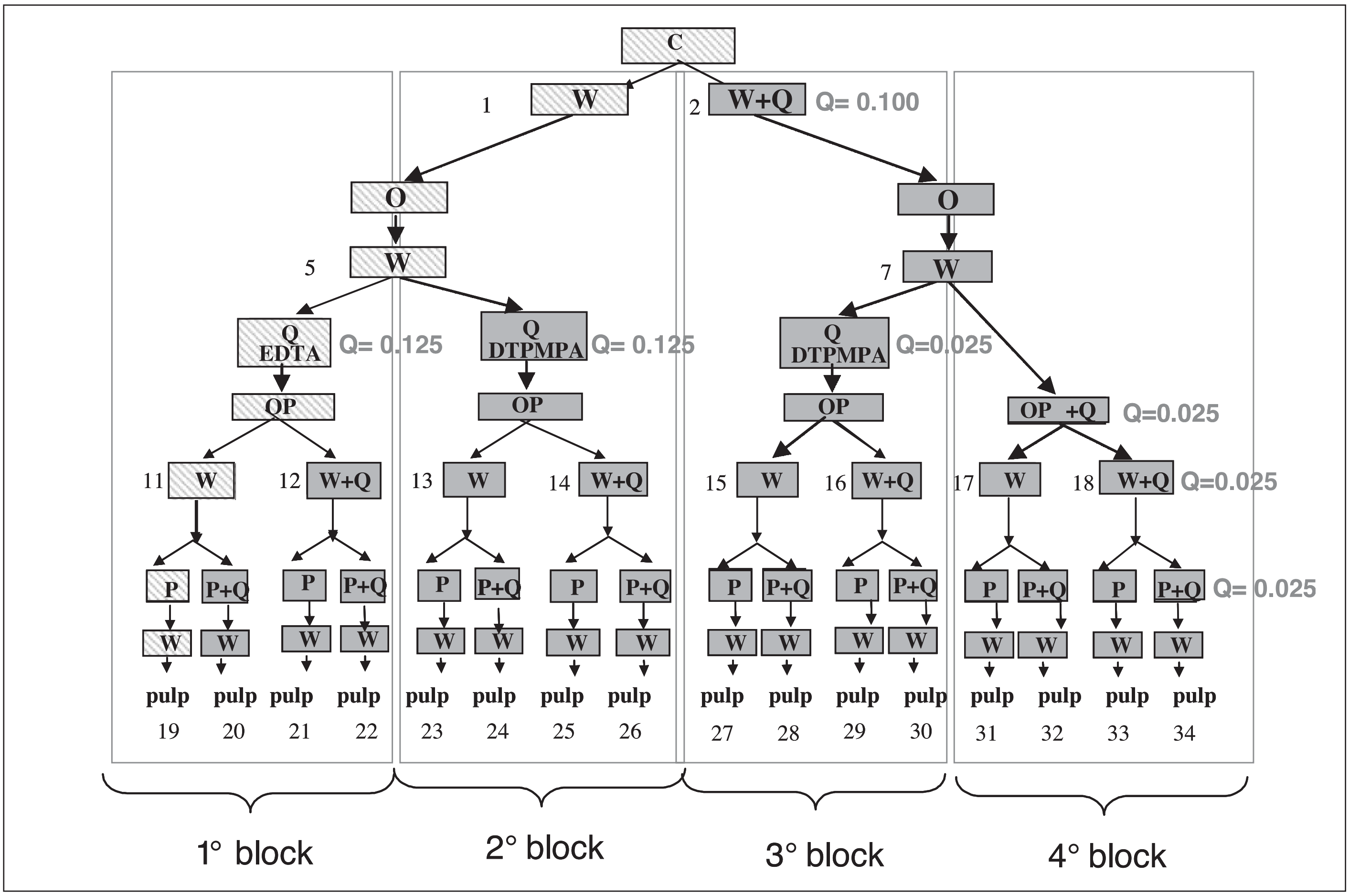

Fig. 1 Experimental plan for eucalypt TCF bleached pulps (EDTA% and DTPMPA% odp based on active acid). C = cooking stage; W = washing stage; W + Q = washing stage with chelant added; O = oxygen delignification; Op = oxygen stage reinforced with peroxide; Op + Q = Op stage with chelant added; P = peroxide stage; P + Q = P stage with chelant added; Q = chelant application stage (EDTA or DTPMPA).

Cooking and bleaching

Air dried chips equivalent to 900g oven dried were cooked in an M/K 7 L digester to attain a Kappa number of 16 to 17. Brown stock washing was standardised to obtain similar COD values before the oxygen stage. Cooking and brown stock washing conditions are detailed in a previous work (*3*).

A stainless steel 4.6 L reactor was adapted for oxygen delignification, incorporating special agitation and heating systems. The liquor heating system involved: glycerine recirculation inside a double shaft, heating by 4 electric resistances (400 W each), and control by a digital temperature controller. The high shear agitation system (specially designed to fulfil the blending requirements of the O stage) rotates at a constant speed of 500 r/min. Oxygen is injected in the bottom of the reactor. The washed and centrifuged pulp (300 g o.d.), at 30% stock concentration, was preheated in a microwave oven up to 95°C. Simultaneously, the required NaOH was added to hot water at the same temperature. Total volume of the solution was calculated to reach a final pulp stock concentration of 10%. The reactor was preheated to 105°C and pulp was placed into it. After closing the reactor, it was pressurised to 6 kg/cm^2 (~590kPa) with O_2. Once the time concluded, the reactor was depressurised, and the pulp discharged and centrifuged to a stock concentration of 30%.

The bleaching sequence involved two oxygen stages, the second one reinforced with peroxide (Op). Both oxygen stages and P treatments included 0.05% and 0.1% of $MgSO_4$, respectively.

All centrifuged pulps were washed in a 14 L plastic chest, with manual agitation, at 60°C and 3% stock concentration for 15 minutes. To evaluate the effect of the O stage on pulp chemical and physical properties, pulp samples were extracted after centrifugation.

The chelating stage (Q) was carried out in a 14 L plastic chest with manual agitation. Once the stage concluded, pulps were

Table 2
Bleaching stage conditions.

	O	Op	Q EDTA	Q DTPMPA	P
O_2 Pressure (kg/cm^2)	6	6	–	–	–
Stock concentration (%)	10	10	3	3	10
Temperature (°C)	100	100	60	60	90
Time (min)	30	120	30	30	120
NaOH (odp* %)	2	1	–	–	1.5
H_2SO_4 (odp* %)	–	–	0.3	–	–
H_2O_2 dosed (odp* %)	–	1	–	–	3
Chelant charge (odp* %)	–	–	0.125	0.125	0.025
pH	–	–	5.5	–	–

* on oven dried pulp

centrifuged to 30% stock concentration.

The peroxide stage was carried out on 50 g o.d. pulp in plastic bags. Final pulps were centrifuged to extract spent liquors, neutralised with sodium metabisulfite in a 14 L plastic chest, with manual agitation, at 1.5 % stock concentration, and then thoroughly washed.

Table 2 presents treatment conditions of all bleaching stages.

TAPPI standards were used for most tests (Kappa number, viscosity and physical properties), except Brightness (ISO 3688:1977) and Opacity (ISO 2471:1977).

Metallic ions (Fe, Cu, Mg, and Mn) content in pulps was analysed by atomic absorption spectroscopy (TAPPI T266 om-94).

Results

Table 3 shows metallic ions content in pulps after the Op treatment (entering P stage).

Table 3
Metallic ions content of post-Op pulps washed with and without DTPMPA.

Pulp no.	Mg ppm	Cu ppm	Fe ppm	Mn ppm
11	359	< 0.1	3.79	0.89
12	378	< 0.1	4.30	0.65
13	427	< 0.1	3.52	1.09
14	445	< 0.1	4.71	0.64
15	422	< 0.1	3.65	0.54
16	420	< 0.1	3.11	0.18
17	509	< 0.1	3.53	0.75
18	487	< 0.1	4.06	0.29

Table 4
Chemical properties of final TCF pulps.

Code	Final pH	Residual alkali odp %	Residual H_2O_2 odp %	Consumed H_2O_2 %	Kappa	ΔKappa %	Viscosity cp	ΔViscosity %	ΔKappa* ΔViscosity
19	11.2	0.84	1.49	50.3	7.9	8.14	23.9	7.72	1.05
20	11.0	0.87	2.43	19.0	7.9	8.14	24.0	7.33	1.11
21	11.1	0.81	2.11	29.7	7.9	8.14	23.4	8.59	0.95
22	11.0	0.87	2.65	11.7	8.1	5.81	23.8	7.03	0.83
23	11.1	0.78	1.68	44.0	7.9	8.14	22.8	8.43	0.96
24	10.9	0.84	2.46	18.0	8.1	5.81	23.1	7.23	0.80
25	11.0	0.83	2.10	30.0	8.0	8.04	23.2	6.90	1.16
26	10.9	0.91	2.66	11.3	8.1	6.90	23.4	5.64	1.22
27	11.1	0.77	1.58	47.3	8.0	4.76	22.2	7.88	0.60
28	11.0	0.80	2.21	26.3	8.0	4.76	22.4	7.05	0.68
29	11.0	0.75	1.81	39.7	8.0	4.76	22.8	8.06	0.59
30	10.9	0.78	2.46	18.0	8.0	4.76	22.9	7.66	0.62
31	11.1	0.70	1.43	52.3	8.0	4.76	22.5	7.02	0.68
32	11.0	0.80	2.18	27.3	7.9	5.95	22.5	7.02	0.85
33	11.1	0.78	1.72	42.7	8.0	4.76	22.2	8.64	0.55
34	10.9	0.86	2.37	21.0	8.0	4.76	22.5	7.41	0.64

Table 5
Optical properties of final TCF pulps.

Code	Brightness %ISO	L*	a*	b*	Opacity %	Bleaching efficiency Δbrightness%/ΔH_2O_2%	Brightness loss % ISO	PCN*
19	81.5	96.5	-0.56	7.34	83.7	0.16	0.97	0.25
20	81.9	96.5	-0.64	7.11	83.5	0.46	1.05	0.27
21	82.0	96.5	-0.63	7.07	83.3	0.18	1.16	0.30
22	84.0	97.1	-0.80	6.53	83.3	0.68	1.78	0.40
23	82.0	96.6	-0.62	7.26	83.9	0.18	1.19	0.30
24	82.2	96.6	-0.67	7.06	83.0	0.46	1.23	0.31
25	82.1	96.6	-0.70	7.15	83.2	0.15	1.17	0.29
26	84.5	97.2	-0.76	6.49	83.4	0.66	1.67	0.36
27	84.6	97.2	-0.84	6.23	82.3	0.13	1.19	0.25
28	84.8	97.2	-0.71	6.15	81.7	0.24	1.14	0.23
29	84.8	97.3	-0.92	6.41	80.5	0.22	1.66	0.35
30	84.4	97.1	-0.71	6.29	79.4	0.46	0.97	0.20
31	84.5	97.2	-0.74	6.34	81.5	0.18	1.52	0.32
32	84.9	97.4	-0.88	6.43	80.8	0.36	1.78	0.37
33	84.5	97.2	-0.80	6.35	81.3	0.20	1.46	0.31
34	84.9	97.4	-0.87	6.39	81.1	0.44	1.31	0.27

* Post-colour number: (PCN) = 100[reverted (k/s) - initial (k/s)], where k/s calculated from Kubelka Munk equation, with R_∞ measured at 457 nm.

Table 6
Physical-mechanical properties of final TCF pulps.

Code	Bulk cm³/g	Tear index mN.m²/g	Burst index kPa.m²/g	Tensile index Nm/g	Air resistance s
19	1.85	6.89	1.91	31.7	1.54
20	1.83	7.24	1.84	32.9	1.46
21	1.84	6.92	1.92	32.3	1.45
22	1.88	7.15	1.93	32.7	1.47
23	1.84	6.38	2.07	35.0	1.69
24	1.88	6.52	1.97	33.4	1.43
25	1.90	7.11	1.88	32.4	1.53
26	1.83	7.63	2.07	35.2	1.55
27	1.62	6.98	2.13	31.4	2.14
28	1.60	9.43	1.99	30.7	1.92
29	1.61	8.10	2.11	31.3	1.98
30	1.56	8.45	2.04	32.4	1.93
31	1.59	9.10	2.15	36.1	2.11
32	1.57	8.50	2.10	36.1	1.98
33	1.62	9.27	2.14	35.6	2.00
34	1.59	9.11	1.98	33.9	1.87

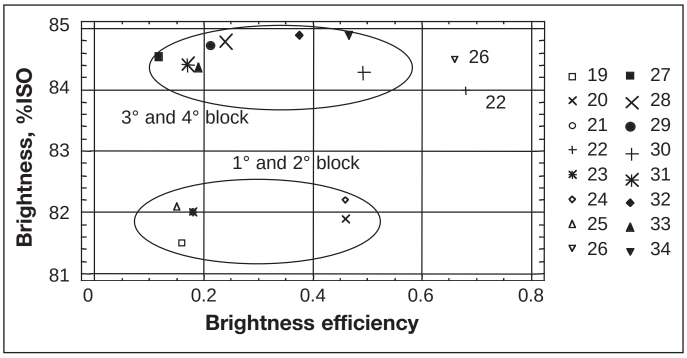

Fig. 2 Brightness (% ISO) vs. brightness efficiency (Δ brightness%/Δ consumed H_2O_2%).

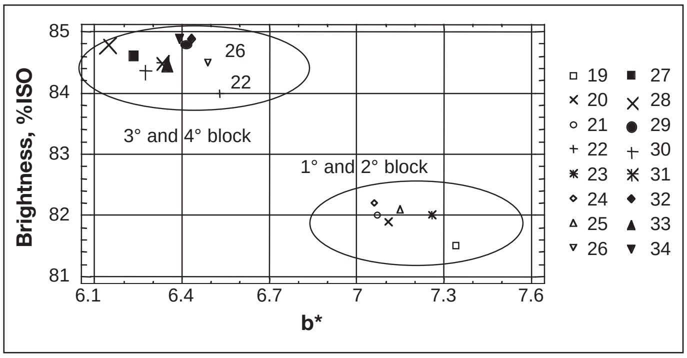

Fig. 3 Brightness (% ISO) vs. colour parameter b* yellow tendency).

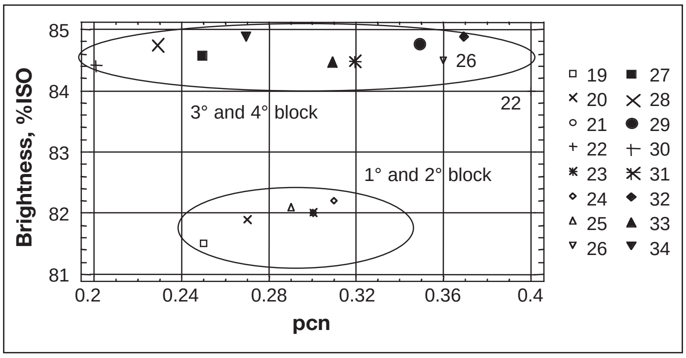

Fig. 4 Brightness (% ISO) vs. post colour number (reversion indicator).

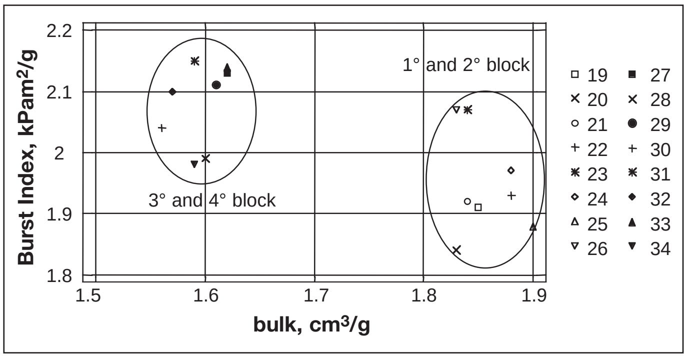

Fig. 5 Burst index (kPa.m²/g) vs. bulk (cm³/g)

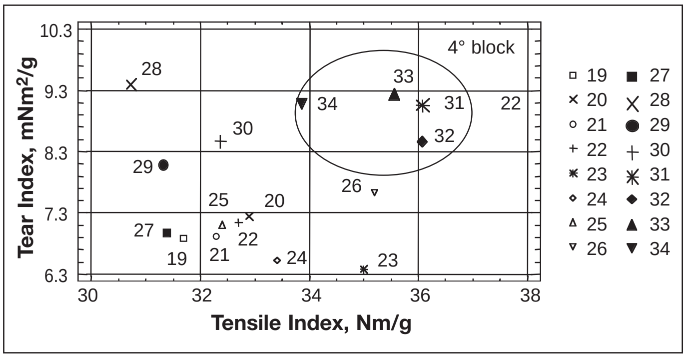

Fig. 6 Tear index (mN.m²/g) vs. tensile index (Nm/g)

DISCUSSION

Optical properties and hydrogen peroxide consumption

Variance Components Analysis of consumed hydrogen peroxide in the P stage indicates that 100% of the variation is due to DTPMPA present in the P stage.

When the P stage incorporates DTPMPA, less peroxide is consumed, and pulps are better bleached, as demonstrate in Figure 2. Peroxide consumption differences are important, and economies produced by recirculating the residual to previous bleaching stages (Op stage) should be evaluated.

High peroxide residuals cannot be attributed to metallic ions amount in pulps, as it is very low in this stage (Table 3). It seems therefore that the chelant acts to stabilising the peroxide.

Bleaching efficiency statistical analysis reveals that 100% of the variation relates to chelant present in the P stage.

Most pulps of the 3rd and 4th block (brown stock washed with chelant) show low bleaching efficiency, (Fig. 2). Even when these pulps have the highest final brightness, gains are small. However, pulps 30, 32 and 34 show reasonably good bleaching efficiency.

Considering the low peroxide consumptions, it seems that pulp brightness achieved 85% ISO, independently of initial brightness and peroxide loads of the stage.

When analysing variance components for brightness, the O stage is responsible for most of the variation (66%), followed by the P stage (31%), with almost no influence of Op post-washing (3%).

The brightness level is approximately 2.5 ISO points higher in pulps of the 3rd and 4th block (coming from DTPMPA brown stock washing) than in pulps traditionally treated, except for pulps 22 and 26.

Among pulps of the 1st and 2nd block (traditional treatment), only P22 and P26, (with a total chelant load of 0.175 odp %), achieved acceptable brightness gains.

Colour parameter b* (yellow tendency) is lower in pulps of the 3rd and 4th block (P27 to P34, brown stock washed with chelant) while reversion (PCN) is independent of the treatment (Fig. 3 and 4 respectively).

Physical-mechanical properties

Figures 5 and 6 show that pulps of the 3rd and 4th block (P27 at P34) present the best final physical-mechanical properties.

Analysis by chelant load

Table 7 shows a comparison of main features of pulps as compared by chelant charge.

Considering that sequences 31, 32 and 34 lack a Q stage (involving dilution, mixing, thickening, additional piping and pumping) this would allow valuable equipment, maintenance and energy cost savings in a greenfield mill.

P stages present high peroxide residual levels in spent liquors. However, peroxide load cannot be reduced in this stage, since final brightness does not attain the target (85%ISO).

As spent liquors have high chelant residuals, they may be recirculated to other stages of the bleaching scheme (*6*). In fact, in addition to the elimination of intermediate dilutions, partial bleach plant closure is possible by recycling P stage spent liquors to the Op stage.

Even though pulp 31 presents the highest peroxide consumption (52.3%) among selected pulps, P stage spent liquor still has an acceptable peroxide level for recirculation (1.3% odp). As the Op stage peroxide charge is 1 %, the entire requirements for this stage could be fulfilled by recirculation.

The other selected pulps (32 and 34) contain very high peroxide residual. Therefore, the P stage must be optimised (time and temperature), to achieve higher brightness levels with a peroxide residual of about 50%.

By optimising the P stages of sequences 32 and 34, better brightness would be obtained at lower costs (both sequences without Q stage), but pulp 34 chelant load is high.

Pulp 32 is a result of the best sequence. This sequence includes DTPMPA in brown stock washing. Typical industrial arrangements of brown stock washing use rotary (vacuum or pressurised) filters in countercurrent operation. DTPMPA may be added in the last stock dilution chest, at 1 to 3% consistency, stirring for 3 to 5 minutes. As brown stock washing systems usually have 3 or 4 filters, this would provide the required residence time.

Diffusers are usually incorporated as additional brown stock washers. As they usually operate at consistencies of 10 to 12%, chelating equilibrium would require higher retention times. In this case, as DTPMPA is temperature and alkali resistant, the time could be extended by adding the chelant in the continuous digester washing zone where liquid-chip contact is about 2 hours.

Recirculation of P stage spent liquor would also take advantage of the DTPMPA residual. Considering the low amount of metallic ions in the P stage, there would be sufficient chelant still available to keep performing.

Therefore, optimising the P stage of sequence 32 to result in 50% of peroxide residual, and recycling the obtained liquor to the Op stage, high brightness levels and costs savings could be achieved. This could be possible, for example, using a washing press to increase pulp consistency from 10 to 35%. The additional cost of equipment should be considered in this case.

Total peroxide load could be reduced by 25% (eliminating the 1% odp addition in the Op stage). Total chelant load could be reduced by 17 % (0.150 to 0.125% odp by eliminating the 0.025% addition in the Op stage).

High pulp brightness could be attained by increasing the bleaching time, or by adding a second peroxide stage (P or P reinforced by oxygen: Po).

Table 7
Pulp comparison by chelant charge.

Total load	0.125 odp % (19, 23, 27, 31)	0.150 odp % (20, 21, 24, 25, 28, 29, 32, 33)	0.175 odp % (22, 26, 30, 34)
Comments	- Pulp 19 (control, EDTA application in Q stage), presents generally: low brightness, high peroxide consumption and poor physical properties. - Pulps 27 and 31 attain brightness levels near 85% ISO. - Pulp 27 shows low peroxide consumption in comparison with pulp 31. The reason can be the additional washing produced by the Q stage. - On the other hand, pulp 31 shows better physical properties than pulp 27. - As the Q stage is eliminated from pulp 31, this sequence shows great economy.	- All peroxide consumptions are lower when chelant charge is 0.150 odp % than when it is 0.125 odp %. - DTPMPA presence in P stage reduces peroxide consumption. - Pulps of the 3rd and 4th block (brown stock washed with chelant) present brightness levels 2.5 ISO points (average) superior to those of the first and second block. - Previous conclusions about the 3rd and 4th block can be extended to all physical properties. - Pulps 28 and 32 reach high brightness levels (about 85 %ISO), with low peroxide consumptions. Pulp 28 presents lower tensile and burst strengths, and higher costs (Q stage), than pulp 32.	- These pulps present the lowest hydrogen peroxide consumption of all series, (between 12 and 21 %). - Brightness levels of all pulps exceed 84 %ISO. - Physical properties are generally good, with pulps 26 and 34 better than the others. - Sequence 26 includes Q stage equipment costs.
Pulp selection	- Pulp 31	- Pulp 32	- Pulp 34

Conclusions

The control pulp (EDTA application in the Q stage), presents generally low brightness, high peroxide consumption, and inferior physical properties compared with the other options studied.

In TCF bleaching of eucalypt kraft pulps, Mn and Fe content in pulps are not statistically different when applying a Q stage with the same quantity of EDTA or DTPMPA. As pulp acidification is not needed when using DTPMPA, the bleaching strategy is simplified in the last case.

Metals removal is more efficient when chelant load is distributed between stages than when applied only in a Q stage. This last strategy preserves Mg levels.

The best choice includes DTPMPA addition in brown stock washing, elimination of the Q stage, DTPMPA in the Op stage, and DTPMPA in the P stage. Optimising the P stage of this sequence can result in 50% peroxide residual, which can be recycled to the Op stage giving both high brightness levels and cost savings.

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