

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Wood Chemistry and Technology

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597282>

### Effect of Acid Leaching of Eucalyptus Wood on Kraft Pulping and Pulp Bleachability

Erica Moreira<sup>a</sup>; Jorge L. Colodette<sup>b</sup>; José L. Gomide<sup>b</sup>; Rubens C. Oliveira<sup>b</sup>; Adair J. Regazzi<sup>b</sup>; Vera M. Sacon<sup>c</sup>

<sup>a</sup> Celulose Nipo-Brasileira S/A, Belo Oriente, MG, Brazil <sup>b</sup> Federal University of Viçosa, Viçosa, MG, Brazil <sup>c</sup> Pulping Group, Votorantim Celulose e Papel, SP, Brazil

**To cite this Article** Moreira, Erica , Colodette, Jorge L. , Gomide, José L. , Oliveira, Rubens C. , Regazzi, Adair J. and Sacon, Vera M.(2008) 'Effect of Acid Leaching of Eucalyptus Wood on Kraft Pulping and Pulp Bleachability', *Journal of Wood Chemistry and Technology*, 28: 2, 137 – 152

**To link to this Article:** DOI: 10.1080/02773810802125073

**URL:** <http://dx.doi.org/10.1080/02773810802125073>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Effect of Acid Leaching of Eucalyptus Wood on Kraft Pulping and Pulp Bleachability

Erica Moreira,<sup>1</sup> Jorge L. Colodette,<sup>2</sup> José L. Gomide,<sup>2</sup>  
Rubens C. Oliveira,<sup>2</sup> Adair J. Regazzi,<sup>2</sup> and Vera M. Sacon<sup>3</sup>

<sup>1</sup>Celulose Nipo-Brasileira S/A, Belo Oriente, MG, Brazil

<sup>2</sup>Federal University of Viçosa, Viçosa, MG, Brazil

<sup>3</sup>Pulping Group, Votorantim Celulose e Papel, SP, Brazil

**Abstract:** This work evaluated the impact of chip acid leaching prior to kraft cooking on pulp yield bleachability and strength properties. Optimal leaching time, temperature, and pH (3 h, 70°C, and pH 2.0) were used to leach wood chips prior to kraft cooking, followed by oxygen delignification, ECF, and light-ECF bleaching with the sequences AZDP (0.19% ClO<sub>2</sub>), AZDP (0.76% ClO<sub>2</sub>), and A/Z/EDP (1.06% ClO<sub>2</sub>). Acid leaching significantly reduced the metals content of the wood chips. Time and pH greatly influenced the metals removal rate, whereas temperature did not. Acid treatment had no effect on cooking yield but improved delignification rate. The pulp from acid leached chips showed improved performance during oxygen delignification and bleaching over the reference pulp. For light-ECF bleaching, chip leaching resulted in H<sub>2</sub>O<sub>2</sub> and NaOH savings of 18 and 14.5 kg/t pulp, respectively. No significant differences in strength properties between the reference and leached pulps were observed.

**Keywords:** Acid leaching, eucalyptus, kraft pulping, metals, pulp properties

### INTRODUCTION

Certain metals are harmful to pulp production processes because they can negatively affect process chemistry and efficiency as well as pulp properties and black liquor recovery. They come mostly from the wood and their content varies widely depending on the species, age, and bark content in chips.

Interest in the presence of non-process elements (NPEs) such as Al, Ca, Ba, Cd, Cl, Cu, Fe, K, Mg, Mn, P, and Si in kraft pulps emerged when TCF bleaching became more common in pulp mills. In practice, transition

Address correspondence to Erica Moreira Pimenta, Rua Inconfidência Mineira, 67/302 Ipatinga, MG, Brazil 35162-375. E-mail: erica\_m@bol.com.br

metals such as iron, manganese, and copper have harmful effects in the TCF process, but many other transition metals are catalytically active and can cause decomposition of oxygen-derived oxidants used in the bleached pulp production.

Transition metal ions are very harmful in peroxide bleaching<sup>[1–5]</sup> because they catalyze peroxide decomposition, wasting reagent and leading to formation of radicals that degrade fibers. Transition metals are also undesirable in oxygen bleaching due to degradation of peroxides generated in this process.<sup>[5–7]</sup> Besides the damage caused during bleaching, transition metals participate in various oxidation reactions that are able to color the pulp. Both iron and aluminum limit brightness gain and increase reversion.<sup>[8,9]</sup> In the recovery cycle, the accumulation of some of these substances increases recovery boiler load and can cause scale formation in the digester and black liquor evaporators.<sup>[6,10–13]</sup> Potassium and chloride are notorious for their acceleration of recovery boiler plugging due to formation of sticky ash.<sup>[5]</sup>

The better understanding of the harmful effects of NPEs in bleached pulp manufacturing has led to the development of alternatives for removing them from the process, in order to increase pulp yield and bleachability, and minimize recovery boiler problems.

One way to remove these NPEs before they enter the process would be the acid leaching of wood chips, which has proven to be a very effective technique in reducing damage caused by metals,<sup>[14–19]</sup> without decreasing pulp quality<sup>[19]</sup> and allowing recirculation of bleaching filtrates to the recovery area.<sup>[17]</sup>

The aim of this study was to investigate the effect of acid leaching of eucalyptus wood chips during pulping and bleaching stages, and analyze its effects on the pulp strength properties.

## EXPERIMENTAL

Industrial *Eucalyptus spp.* wood chips with basic density of 464kg/m<sup>3</sup> were used. These chips were divided into two samples, one was acid leached and both leached and reference chips were studied.

Optimization of acid leaching conditions was carried out using a 3<sup>3</sup> factorial experimental design (temperature: 50, 70, and 90°C; time: 1, 3, and 5 h; pH: 1.5; 2.0; and 2.5) with each of the 27 runs performed in duplicate. The reaction was run at 10:1 liquor to wood ratio with 100 g (dry basis) chip samples. The samples were placed in plastic grids and autoclaved with deionized water until reaching the moisture content typical of industrial chips (~50%). Preliminary tests indicated that this moisture content is reached after approximately 12 h in the autoclave under 100 kPa negative pressure. After this preparatory step, chips were placed in polyethylene bags, the preheated acid solution, prepared with deionized water was added and the bags were placed in a steam bath at constant temperature, for the desired reaction time. Following, the excess acid

**Table 1.** Cooking conditions

Chips, g 100% dry	250
Sulfidity, %	30
Active Alkali, % as NaOH	Variable
Liquor/wood ratio, L/kg	4/1
Maximum temperature, °C	170
Time to maximum temperature, min	90
Time at maximum temperature, min	50

solution was drained out from the chips and analyzed to quantify the amount of leached metals and organic matter. After drainage the chips had a moisture content of about 50% and they were cooked at such condition. A fraction of the chips was dried and weighed to estimate mass loss. Metals and organic matter contents were analyzed in filtrates by atomic absorption spectrophotometry (AAS) and TOC techniques, respectively. The condition that maximized metals removal and minimized TOC removal was used to treat a larger amount of chips for further study.

A comparative study on pulping performance, and bleachability and strength properties of pulps produced from leached and non-leached (reference) chips was then carried out. Conventional kraft cooking was carried out in a 20 L rotary digester with electrical heating and four individual 2 L vessels. All tests were performed using the same conditions, except that the alkaline charge (as NaOH) was 18% for leached and 18.5% for reference chips, in order to reach a kappa number of  $17 \pm 0.5$  for both. The cooking conditions used are detailed in Table 1. The moisture contents of the acid leached and reference chips were adjusted to similar values before the kraft cooking.

Three different sequences were used to bleach the pulp: AZDP, with 0.19 (sequence 1) and 0.76%  $\text{ClO}_2$  (sequence 2), and A/Z/EDP, with 1.06%  $\text{ClO}_2$  (sequence 3). The general bleaching conditions used in each stage of these three sequences are shown in Table 2. All bleaching stages were carried out in duplicate. Inter-stage washings simulated a vacuum filter operating at a dilution factor of two (inlet and outlet consistencies of 2% and 12.5%, respectively).

Medium consistency ozone bleaching was carried out with 300 g o.d. (oven dried) pulp sample in a teflon-lined mixer/reactor (Quantum Technologies, model Mark V) equipped with an ozone compression system (ozone Cart) and controls for pressure, temperature, and pH. The acidified pulp was added to the reactor at the desired temperature and ozone was injected through the compression system. After the pre-established reaction time elapsed, the reactor pressure was released, the pulp was discharged into a 120 mesh screening box and 300 mL of liquor were squeezed from the pulp for analysis. Ozone residuals

**Table 2.** General bleaching conditions

Condition	Bleaching stage					
	O	A	Z	A/Z/E	D	P
Time, min	60	120	1	15/1/15	60	90
Temperature, °C	100	95	40	60/40/60	85	90
Pressure, kPa	500	—	600	0/0/0	—	250
Consistency, %	10	11	11	11/37/11	11	11
End pH	11.2	2.5	2.7	2.5/2.7/10	3.8	10.3
H <sub>2</sub> O <sub>2</sub> , kg/t	20	—	—	—	—	**
H <sub>2</sub> SO <sub>4</sub> , kg/t	—	7	5	7/0/11	*	—
NaOH, kg/t	20	—	—	—	*	—
MgSO <sub>4</sub> ·7H <sub>2</sub> O, kg/t	3	—	—	—	—	2
O <sub>3</sub> , kg/t	—	—	4	0/5.5/0	—	—
ClO <sub>2</sub> , kg/t	—	—	—	—	0.19;0.76;1.06	—

\*Adjusted to desirable end pH.

\*\*Adjusted to desirable final brightness.

were monitored by UV in the exhausting gases. High consistency ozone treatment was effected with 30 g o.d. fluff pulp in a rotating glass reactor. Pulp fluffing was achieved in a stainless steel bench scale fluffer manufactured by Impco Co. Chlorine dioxide (D), alkali extraction (E), and hydrogen peroxide (P) bleaching stages were performed in polyethylene bags. In all cases, the required amounts of water and reagents were mixed with the pulp at room temperature and the mixtures heated to the desired temperature in a microwave oven. The samples were then placed in a heating bath for the desired reaction time.

At the end of the bleaching process, the pulp was diluted to 0.3% consistency, the pH was adjusted to 5.5–6 with SO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>, and hand sheets were formed and dried for 12 h to 9–10% humidity in an environmentally controlled room (50 ± 2% relative humidity and 23 ± 1°C). Pulp kappa number, viscosity, and brightness were measured according to TAPPI T236 cm-85, T254 cm-85, and T525 om-82 standard procedures, respectively. Pulp hand sheet formation was effected according to TAPPI T272 sp-97.

The total active chlorine charges required to achieve full brightness are presented in Table 3. The brightness targets were 88.0 ± 0.5 %ISO in sequence 1 and 90.0 ± 0.5 %ISO in sequences 2 and 3. Final brightness targets were reached by adjusting the hydrogen peroxide charges in the final P-stage. After bleaching, pulps were refined to different levels in a PFI mill and their strength properties were evaluated according to TAPPI standard procedures. Statistical models were adjusted [property = f (tensile index)] and tested for their identities with the F-Test using the Statistica software.

**Table 3.** Total active chlorine charges (kg/t dry basis)\* required for bleaching

Sequence 1		Sequence 2		Sequence 3	
Ref.	Leached	Ref.	Leached	Ref.	Leached
77.5	38.7	51.6	43.2	65.2	61.3

\*Total active chlorine:  $2.63*(\text{ClO}_2, \text{kg/t}) + 4.44*(\text{O}_3, \text{kg/t}) + 2.09*(\text{H}_2\text{O}_2, \text{kg/t})$ .

## RESULTS AND DISCUSSION

### Optimization of Acid Leaching Conditions

The contents of seven non-process elements (NPEs) and total ash quantified in the reference chips (not leached) are listed in Table 4. Figure 1 shows average metals removal values obtained in acid chip leaching as a function of temperature, pH, and time, respectively.

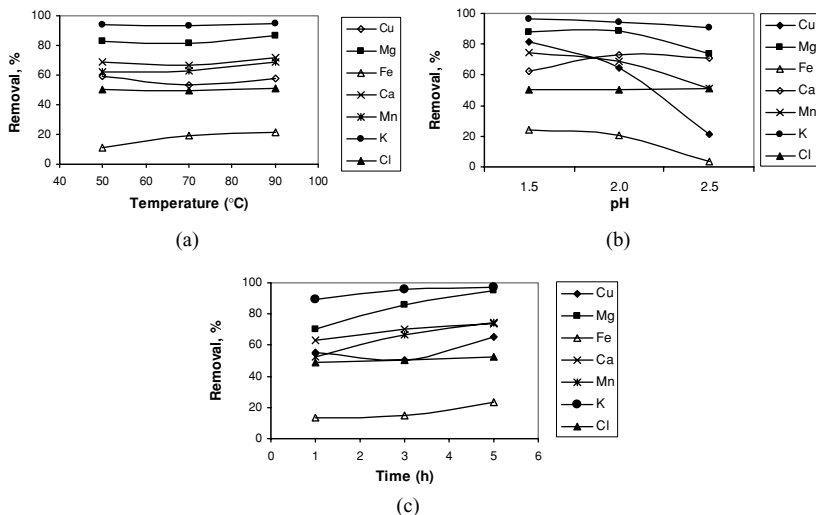
As can be seen in Figure 1a, temperature had the least effect on metal removal. On the other hand, pH (Figure 1b) and time (Figure 1c) had large effects on removal. Organic matter loss during acid leaching (Figure 2) increased greatly under the most severe conditions used: 5 h, 90°C, and pH 1.5. Based on these results, it was decided that chip leaching should be carried out using the intermediate test conditions: 70°C, 3 h, and pH 2.0.

Metals removal was relatively high; more than 60% removal was achieved in most cases, but it should be noted that about 11% of leached metals remained associated with the chips in all cases (Figure 3). Although the chips were dewatered for removing excess acid solution, which contained the leached metals, the chips still had a moisture content of about 50%. Thus, effective metals leaching was 11% lower than presented in Figure 1 because leached metals were carried over within the moist chips.

Potassium presented the highest removal rate (>85%), followed by magnesium (80%), calcium (65%), manganese (60%), and copper (40%). Iron was the most difficult metal to remove, probably because of its ability to form complexes with wood components.<sup>[20]</sup> Chloride concentration was reduced by almost 50%. Although chloride is not a metal it was included in this study given its great relevance for the black liquor recovery processes and for corrosion in general.

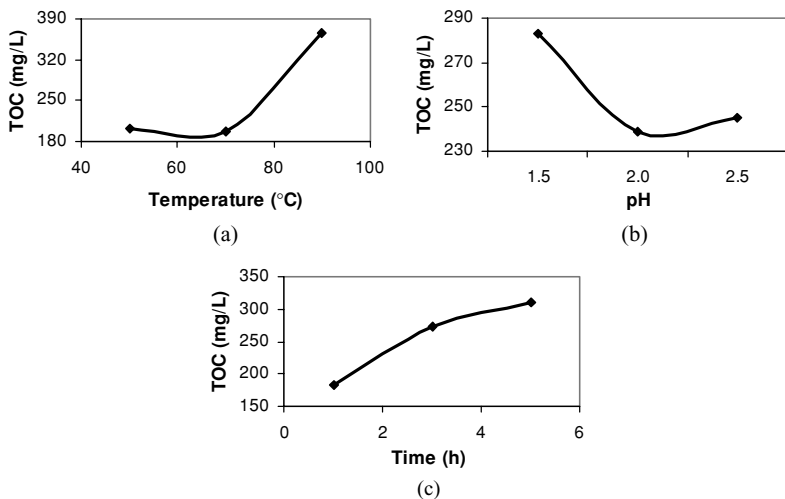
**Table 4.** NPEs concentration in the original chips (not leached)

NPEs concentration in chips (mg/kg)							
Cu	Mg	Fe	Ca	Mn	K	Cl	Total ash
3.69	65.43	9.62	151.3	26.44	323.5	556	2524

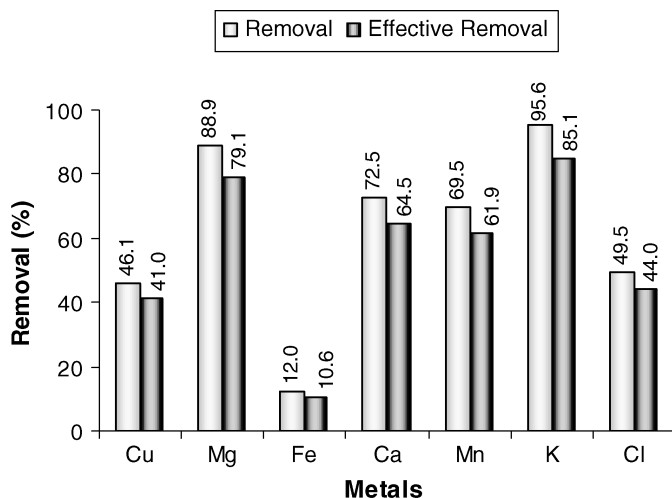


**Figure 1.** Effect of temperature at pH 2 for 3 h (a), of pH at 70°C for 3 h (b), and of time at pH 2 and 70°C (c) on metals removal during acid leaching.

The removal of magnesium is undesirable given its importance in the pulp for carbohydrate protection in oxygen-based bleaching processes. Magnesium causes dismutation of superoxide radicals, thus minimizing propagation of free radical chain reactions and the formation of certain harmful free



**Figure 2.** Effect of temperature at pH 2 for 3 h (a), of pH at 70°C for 3 h (b), and of time at pH 2 and 70°C (c) on organic matter removal during acid leaching.



**Figure 3.** Effective metals removal during acid leaching under selected conditions: 3 h, 70°C, and pH 2.0.

radicals.<sup>[21]</sup> These radicals, particularly hydroxyl radical, cause carbohydrate degradation.

As shown in Table 4, acid leaching did not degrade significant fractions of the wood. Similar results have been reported by Breliid,<sup>[19]</sup> who encountered only small amounts of carbohydrates in the leaching liquor after acid treatment at pH 2 and 100°C for 2 h. The most significant loss was in the glucan fraction. The total weight loss during acid leaching was 1.8% under the optimized conditions. Note that the 1.8% (18 kg/t) wood weight loss after leaching comes from NPEs removal plus organic matter. It was not possible to estimate exactly how much of the 18 kg/t wood loss derived from NPEs and from organic matter. However, it is anticipated that NPEs account for very little of this total loss considering that the total chip ash content was 2.5 kg/t wood (Table 4) and that not all NPEs were actually removed from the chips during leaching (Figure 3). The most significant loss likely came from organic matter. The total organic carbon measurement (TOC) taken on the acid leachate (70°C, 3 h, pH 2) was 207 mg C/L of leachate or 2.07 kg C/t of wood (0.21%) or 3.9 kg C/t of pulp assuming the pulping yield of 53.1% (Table 5). The elemental analysis of various eucalyptus wood samples reveals an average carbon composition in the range of 48% of total dry weight.<sup>[22]</sup> Hence, a 2.07 kg C/t wood loss would represent about 4.3 kg/t organic matter loss, if the material dissolved contained the actual wood carbon composition. That was obviously not the case in this study since a total loss of 18 kg/t wood was observed. Very likely, the material lost during the acid leaching derived from highly oxygenated substances such as sugars, glucans, starch, and low



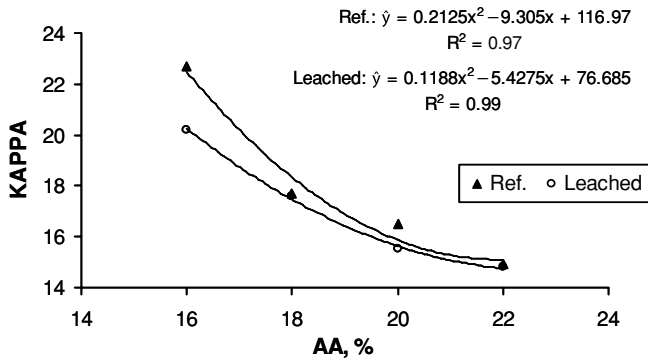
**Table 5.** Effect of acid leaching of chips on wood chemical composition (% dry weight)

Component, %	Ref.	Leached
Glucans	51.80	53.06
Xylans	10.04	9.85
Galactans	1.32	1.13
Arabinans	0.51	0.39
Mannans	1.18	0.80
Soluble lignin	4.17	4.37
Insoluble lignin	23.19	22.71
Total lignin	27.36	27.07
Acetyl groups	2.44	2.39
Total uronic acids	5.36	5.32
Total yield loss	—	1.8
TOC	—	0.21

molecular weight polysaccharides and minimally from carbon rich components such as lignin and steryl esters.

#### Kraft Cooking

The rate of delignification was slightly higher for the acid leached chips as shown in Figure 4. In other words, for a given kappa number, a lower demand

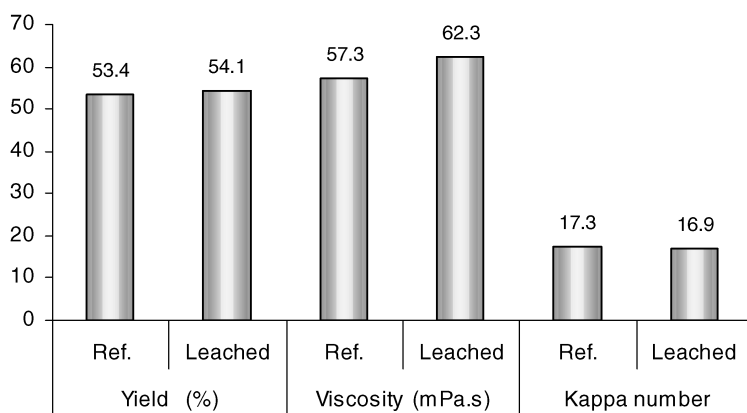


	AA %	Kappa average	St.Dev.
Ref.	16	22.7	0.32
	18	17.7	0.25
	20	16.5	0.24
	22	14.9	0.21
Leached	16	20.2	0.25
	18	17.6	0.22
	20	15.5	0.19
	22	14.8	0.18

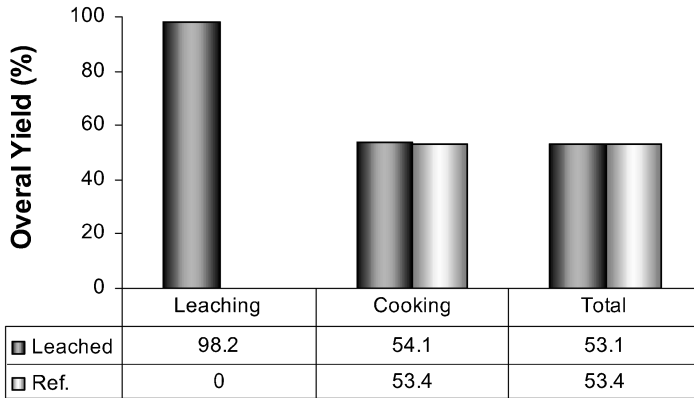
**Figure 4.** Effect of the active alkali (AA) charge (% as NaOH) on pulp kappa number for reference and acid leached chips.

of active alkali was observed for these chips in relation to the reference ones. Such result was unexpected because the acid leached chips had a lower pH than the reference ones before pulping. The leaching process required about 5 kg of  $H_2SO_4$  per ton of dry chips, applied at the 10:1 liquor to wood ratio. A large fraction (89%) of this acid was actually drained out from the chips before kraft cooking, remaining in the chips only the equivalent to 0.55 kg  $H_2SO_4$  per ton. This acid amount was responsible for consuming about 0.45 kg of NaOH per ton of wood or 0.05% active alkali. Hence, a slight increase in the active alkali demand was anticipated for the acid leached chips but it did not occur. A possible explanation for the decreased alkali requirement is the removal of NPEs, especially calcium, and of other organic materials from the wood chips during acid leaching. These materials may consume significant amounts of alkali. The breakage of wood lignin-carbohydrate bonds in the acid treatment may also explain the lower active alkali demand in the subsequent cooking. Cleavage of lignin-hemiceluloses bonds by acid treatment of wood has been reported elsewhere.<sup>[23]</sup> Lignin-carbohydrate complexes show low reactivity toward alkali and their removal prior to kraft cooking can decrease overall active alkali demand.

The pulp derived from leached chips (Leached) showed higher yield and viscosity than that of the pulp resulting from reference chips (Ref), for similar kappa number values (Figure 5). Thus, it is apparent the kraft cooking is more selective for acid leached chips. One of the possible explanations is the calcium removal in the leaching process. Calcium is known to hamper the rate of delignification and the selectivity of the kraft cooking process.<sup>[24]</sup> However, if the weight loss (1.8%) after chip leaching step is taken into account, the overall process yield becomes quite similar to that of the reference (Figure 6). In other words, the cooking yield benefits due to chip leaching are offset by the weight losses across acid leaching itself.



**Figure 5.** Kraft cooking results for reference (Ref.) and acid leached chips (Leached).

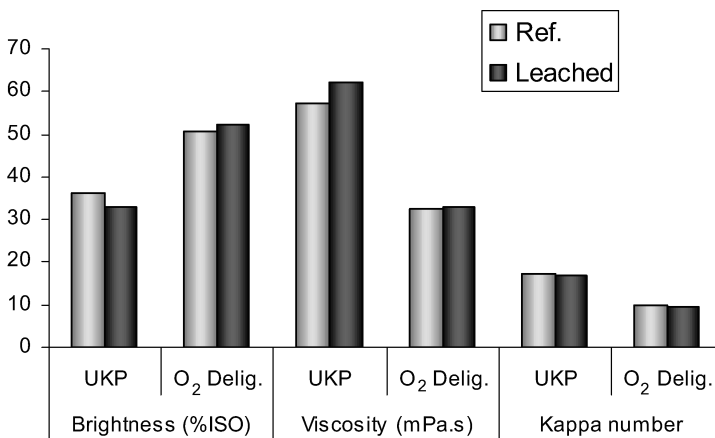


**Figure 6.** Overall yields across chip leaching and kraft cooking (Ref: pulp from untreated chips; Leached: pulp from acid leached chips).

More recent acid leaching studies carried out in our laboratories (not yet published) using lower liquor to wood ratio (3.5/1) have indicated much lower yield losses ( $\sim 0.8\%$ ) after leaching. It is apparent that the 10/1 liquor to wood ratio used in this particular study was way too high and harmful to yield.

### Oxygen Delignification

In the oxygen delignification larger kappa number reduction and brightness gain for the pulp derived from acid leached chips was observed in comparison with the reference (Figure 7). A probable explanation for the greater brightness gain



**Figure 7.** Results after oxygen delignification of pulps from acid leached and reference chips (UKP: unbleached kraft pulp; O<sub>2</sub> Delig.: oxygen delignified pulp).

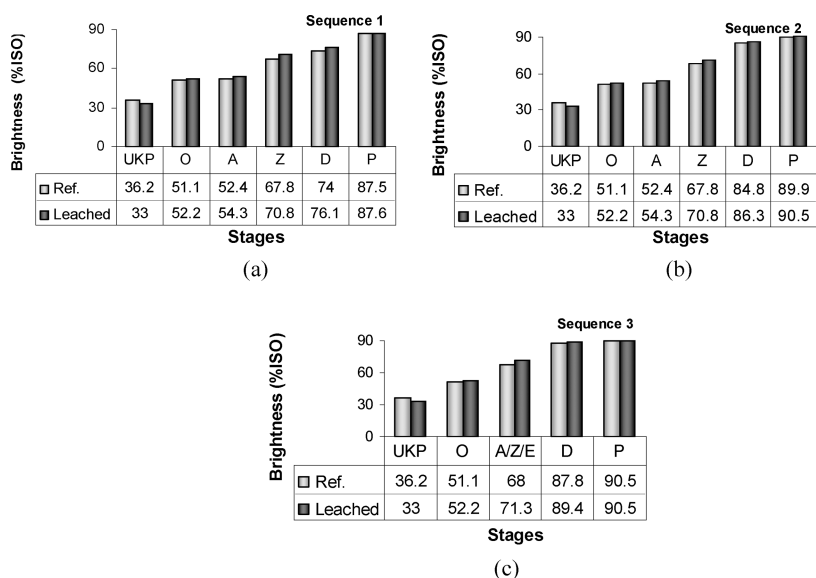
**Table 6.** Metals content in the unbleached pulps (mg/kg pulp)

Pulp	Cu	Fe	Mn	Mg
Ref.	5.37	36.2	13.1	218
Leached	4.48	21.8	8.7	136

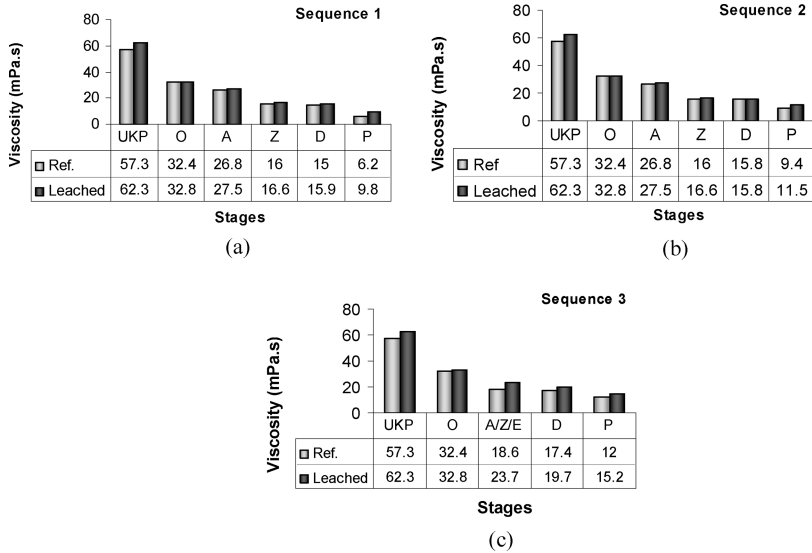
is the lower transition metals content present in the former pulp (Table 6), which resulted in lower peroxide decomposition. A four percent greater viscosity loss was observed for the pulp derived from leached chips, which may be explained by the removal of magnesium from the wood during the acid leaching operation. Magnesium is known to prevent viscosity losses during the oxygen delignification.<sup>[25]</sup>

### Pulp Bleaching

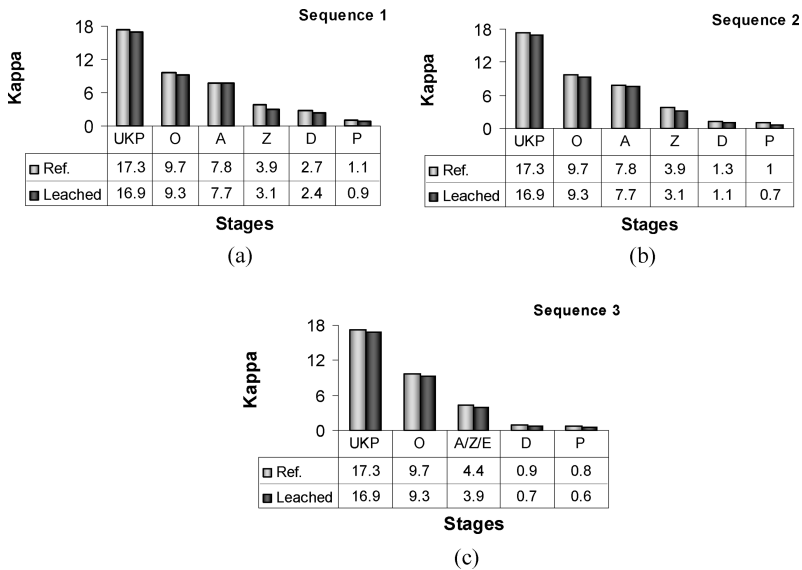
Figures 8, 9, and 10 show the brightness, viscosity, and kappa number profiles during pulp bleaching by the three sequences studied. Although acid leached chips resulted in pulp of lower brightness, such pulp developed greater brightness during bleaching. The higher brightness gains obtained with the pulps



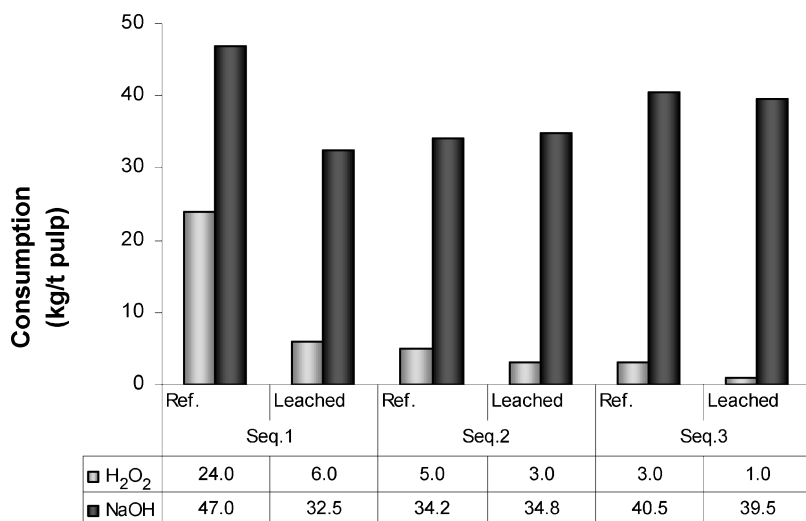
**Figure 8.** Pulp brightness profiles (%ISO) during bleaching (a—AZDP, 0.19% ClO<sub>2</sub>; b—AZDP, 0.76% ClO<sub>2</sub>; c—A/Z/EDP, 1.06% ClO<sub>2</sub>; REF: pulp from untreated chips; Leached: pulp from acid leached chips; UKP: unbleached kraft pulp).



**Figure 9.** Pulp viscosity profiles (mPa.s) during bleaching (a—AZDP, 0.19% ClO<sub>2</sub>; b—AZDP, 0.76% ClO<sub>2</sub>; c—A/Z/EDP, 1.06% ClO<sub>2</sub>; REF: pulp from untreated chips; Leached: pulp from acid leached chips; UKP: unbleached kraft pulp).



**Figure 10.** Pulp kappa number profiles during bleaching (a—AZDP, 0.19% ClO<sub>2</sub>; b—AZDP, 0.76% ClO<sub>2</sub>; c—A/Z/EDP, 1.06% ClO<sub>2</sub>; REF: pulp from untreated chips; Leached: pulp from acid leached chips; UKP: unbleached kraft pulp).



**Figure 11.** Hydrogen peroxide and sodium hydroxide demands to reach the target brightness three different sequences (Seq. 1—AZDP, 0.19% ClO<sub>2</sub>; Seq. 2—AZDP, 0.76% ClO<sub>2</sub>; Seq. 3—A/Z/EDP, 1.06% ClO<sub>2</sub>; Ref.: pulp from untreated chips; Leached: pulp from acid leached chips).

from leached chips likely derives from less bleaching oxidant losses caused by transition metal induced decomposition. Leaching also had a positive effect on viscosity preservation and kappa number reduction during bleaching. For all three sequences the control of the final brightness to the desired value was achieved by playing with the hydrogen peroxide and sodium hydroxide doses in the last peroxide bleaching stage. The savings of these two chemicals due to chip leaching were significant for all three sequences (Figure 11), but much substantial for the light-ECF one (OAZDP with 0.19% ClO<sub>2</sub>). The gains were higher for this sequence because of its low use of ClO<sub>2</sub>, an oxidant little influenced by transition metals, and its high use of H<sub>2</sub>O<sub>2</sub>, a chemical that is highly impacted by transition metals. Low dose of ClO<sub>2</sub> and high dose of H<sub>2</sub>O<sub>2</sub> is exactly what characterizes a light-ECF bleaching, which has as consequence a pulp containing low amounts of organically bound chlorine and low viscosity.

**Strength Properties**

The bleached pulp strength properties at a tensile index of 70 N.m/g are presented in Table 7. No significant differences in strength properties were observed among bleached pulps derived from acid leached chips and reference

**Table 7.** Physical properties of bleached pulps, corresponding to a 70 N.m/g tensile index

Physical property	AZDP, 0.19% ClO <sub>2</sub>		AZDP, 0.76% ClO <sub>2</sub>		A/Z/EDP, 1.06% ClO <sub>2</sub>	
	Leached	Ref.	Leached	Ref.	Leached	Ref.
Refining energy, w.h	16.8	16.5	18.6	18.2	23.4	22.9
Drainage degree, °SR	29.1	31.0	31.0	28.2	28.1	29.0
Burst Index (kPa.m <sup>2</sup> /g)	3.22	3.21	3.53	3.24	3.13	3.30
Tear Index (mN.m <sup>2</sup> /g)	13.4	13.4	12.3	12.6	11.6	11.8
Air resistance (s/100cm <sup>3</sup> )	6.2	7.2	9.7	9.8	10.0	10.1
Density (g/cm <sup>3</sup> )	0.75	0.74	0.72	0.68	0.73	0.73
Bulk (cm <sup>3</sup> /g)	1.36	1.32	1.43	1.43	1.39	1.39
Stretch (%)	4.34	4.34	4.42	4.58	4.58	4.30
Tensile Energy Absorption (J/m <sup>2</sup> )	143.2	143.2	144.4	154.2	153.0	143.9
Tensile Stiffness Index (MN.m/kg)	5.68	5.68	5.66	5.66	5.78	5.78

pulps, regardless of the bleaching process. However, the bleaching process itself had some significant effect on certain pulp properties. For example, tear indexes were slightly lower for the pulps (Ref. and Leach.) bleached with sequence 3 (A/Z/EDP with 1.06% ClO<sub>2</sub>) whereas pulps samples bleached with sequence 1 showed the lowest values of air resistance, that is, they were more porous. The energy consumption required during refining to achieve a pulp tensile index of 70 N.m/g and the pulp drain ability were not influenced by chip leaching. However, refining energy was significantly influenced by the bleaching process, with highest energy requirements observed for the A/Z/EDP bleached pulp and lowest for the light-ECF one (OAZDP with 0.19% ClO<sub>2</sub>).

## CONCLUSIONS

Acid leaching of eucalyptus wood chips before cooking reduced metals contents considerably. Time and pH greatly affected metals removal efficiency, whereas temperature did not. Loss of organic matter was highly dependent on time, temperature, and pH. Potassium was the most easily removed metal, reaching about 85%, whereas iron was the most difficult, with only 10% removal. Acid leaching slightly increased cooking yield, delignification efficiency, and selectivity. Overall process yield, including weight losses across acid leaching and cooking, was similar for reference and acid leached chips. Pulp derived from acid leached chips performed better during oxygen delignification and bleaching than the reference pulp. Savings of 18 and 14.5 kg/t pulp of H<sub>2</sub>O<sub>2</sub>

and NaOH, respectively, were achieved for the light-ECF bleaching process. Pulp strength properties, drain ability, and refining ability were not significantly affected by chip leaching with acid.

## REFERENCES

1. Kujala, M.; Sillanpa, M.; Rämö, J. A method to leach manganese and some other metal cations from pulp matrix to aqueous phase for the subsequent ICP-AES analysis: A potential tool for controlling the metal profile in a pulp bleaching process. *J. Cleaner Prod.* **2004**, *12*(7), 707–712.
2. Colodette, J.L.; Dence, C. W. *Mecanismo de decomposição e de estabilização do peróxido de hidrogênio no branqueamento de polpas mecânicas*. Symposium conducted at the 21st Congresso Anual de Celulose e Papel da ABTCP. São Paulo, Brazil. November 1988.
3. Lindholm, C. Bleaching. In *Papermaking Science and Technology*, Book 5. Gullichsen, G.; Paulapuro, H., Eds. Fapet, Helsinki, 2000; 313–342.
4. Colodette, J. L. A estabilidade do peróxido de hidrogênio durante o branqueamento de polpa. Parte I: Na ausência de silicato de sódio. *O Papel*, São Paulo, **1990a**, *11*, 80–112.
5. Gullichsen, J. Fiber line operations. In *Papermaking Science and Technology*, Book 6. Gullichsen, G.; Paulapuro, H., Eds.; Fapet, Helsinki, 2000; 196–218.
6. Alen, R. Basic chemistry of wood delignification. In *Papermaking Science and Technology*, Book 3. Gullichsen, G.; Paulapuro, H., Eds. Fapet, Helsinki, 2000; 59–104.
7. McDonough, T. Section IV: *The Technology of Chemical Pulp Bleaching*. Chapter 1: Oxygen Delignification. In *Pulp Bleaching—Principles and Practice*. Dence, C.W.; Reeve, D.W. TAPPI Press. Atlanta, Georgia, 1996; 215–237.
8. Beaudry, A. R. *Manage your metals with a multipurpose chelant*. Symposium conducted at the Pulping Conference, San Diego, CA, November 6–10, 1994.
9. Gupta, V.N. Effect of metal ions on brightness, bleachability and colour reversion of groundwood. *Pulp Pap. Can.*, **1970**, *71*(18), 69–77.
10. Marcoccia, B.; Prough, J.R.; Engström, J.; Gullichsen, J. Continuous cooking applications. In *Papermaking Science and Technology*, Book 6. Gullichsen, G.; Paulapuro, H., Eds. Fapet, Helsinki, 2000; 512–570.
11. Holmlund, K.; Parviainen, K. Evaporation of black liquor. In *Papermaking Science and Technology*, Book 6. Gullichsen, G.; Paulapuro, H., Eds.; Fapet, Helsinki, 2000; 36–94.
12. Vakkilainen, E. Chemical recovery. In *Papermaking Science and Technology*, Book 6. Gullichsen, G.; Paulapuro, H., Eds.; Fapet, Helsinki, 2000; 7–35.
13. Arpalahhti, O.; Engdahl, H.; Jäntti, J.; Kiiskilä, E.; Liiri, O.; Pekkinen, J.; Puumalainen, R.; Sankala, H.; Vehmaan-Kreula, J. White liquor preparation. In *Papermaking Science and Technology*, Book 6. Gullichsen, G.; Paulapuro, H., Eds.; Fapet, Helsinki, 2000; 135–204.
14. Axegard, Peter. *Possibilities for Improving the Pulping Process*. Symposium conducted at the Internacional Colloquium on Eucalyptus Kraft Pulp, Viçosa, Brazil. September 4–5, 2003.



15. Kangas, H.; Robertsén, L.; Vuorinen T. The effect of transition metal ions on the kraft pulping process. *P ja Puu-Paper and Timber*, **2002**, *84* (7), 473–477.
16. Lundqvist, F.; Brelid, H; Eliasson, A.; Tomani, P.; Wadsborn, R. *Improved Process Efficiency by Pre-Treatment of Chips?* Symposium conducted at the 8th International Conference on New Available Technologies, Stockholm. June 10–12, 2005.
17. Lundqvist, F.; Brelid, H.; Salterberg, A.; Gellerstedt, G.; Tomani, P. *Removal of non-process elements from hardwood chips prior to kraft cooking.* Symposium conducted at the 59th Appita Annual Conference and Exhibition, Auckland, New Zealand. May 16–19, 2005.
18. Lindgren, K.; Berglin, N.; Brelid, H. *Effects of the Use of an NPE Chip Kidney in a Closed Bleach Plant.* Symposium conducted at the TAPPI International Pulp Bleaching Conference Portland, WA, May 19–23, 2002.
19. Brelid, H. *Chip Leaching before Cooking.* Symposium conducted at the 7th International Conference on New Available Technologies, Stockholm. May 9–11, 2002.
20. Colodette, J.L.; Rothenberg, S.; Dence, C.W. Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps. 2. Hydrogen peroxide stability in the presence of sodium silicate. *J. Pulp Pap. Sci.*, **1989**, *15* (11), 3–10.
21. Colodette, J.L.; Rothenberg, S.; Dence, C.W. Factors affecting hydrogen peroxide stability in the brightening of mechanical and chemimechanical pulps. 3. Hydrogen peroxide stability in the presence of magnesium and combinations of stabilizers. *J. Pulp Pap. Sci.* **1989**, *15* (11), 45–61.
22. Gomide, J.L.; Colodette, J.L. *Qualidade da Madeira.* In *Biotechnologia Florestal*. Borem, A., Ed.; Suprema Gráfica e Editora Ltda. Viçosa, MG, Brazil; 2007: 25–54.
23. Bolton, T.S.; Francis, R.C.; Amidon, T. E. *Chemical and Physical Changes due to Acidolysis of Chips Ahead of Alkaline Pulping.* International Symposium on Wood and Pulp Fiber Chemistry. Durban, South Africa, June 22–23, 2007.
24. Lundqvist, F.; Olm, L.; Tormund, D. Effects of carbonate on delignification of birch wood in kraft cooking, *Nord. Pulp Pap. Res. J.* **2006**, *21* (3), 290–296.
25. Colodette, J.L.; Gomide, J.L.; Batista, J.C. Efeito de Aditivos na Deslignificação com Oxigênio de Polpa Kraft de Eucalipto. *O Papel.*, 1990, *51*, 25–35.