Stepwise Survey on Oxygen Delignification and Pulp Washing Performance

Edvins Ratnieks, Celso Foelkel, Vera Sacon and Clóvis Zimmer
RIOCELL S.A., 1680 Sao Geraldo, CaixaPostal 108, Guaiba, RS 92500, Brazil

The performance of kraft pulping and oxygen delignification, as measured by means of lignin removal, is discussed under the scope of industrial evaluation and lab trials. Industrial evaluation has indicated that lignin and also extractives leach from the processing pulp in the washing stages. The phenomena is associated with the consecutive alkali charge in-between washing equipments, introduced by the adoption of the oxygen delignification technology. Lab trials and mill experience have been pointing out that both alkaline and mild acid leaching treatments, water quality and metals content of pulp are parameters to consider in the enhancement of pulp delignification and washing operations.

Oxygen delignification has been a successful option for Kraft mills to improve process efficiency, recycling of chemicals and water. However, as a single step, conventional oxygen bleaching is compromised by the competitive reactions with respect to lignin and cellulose. Reference [1]. It has been implemented using moderately high oxygen pressure (above 0.5 MPa gauge), temperature (e.g. 95 °C), consistency (above 10 %), alkali charge (more than 15 kg/t). These variable descriptions suggest a considerable energy expenditure to remove only 50% of lignin when compared with a chlorine bleached pulp of equivalent strength. Reference [2].

The aim of this report is to describe the experience of Riocell eucalyptus kraft pulp mill with oxygen delignification at the industrial level. The behavior of variables such as the Kappa number and brightness of pulp; lignin content, pH, conductivity, colloidal pitch and COD of filtrates were mapped along the kraft pulping and oxygen delignification systems.

One specific target is to demonstrate the efficiency of lignin removal after each unit operation. Another objective is to explain why the mill stopped experiencing pitch problems after oxygen delignification plant start-up.

The laboratory portion of this report describes the results of some trials to better understand the lignin leaching behavior observed at the industrial level. Some of this work was performed to help understand the extent and determine the conditions that favor lignin leaching. The test conditions simulated alkaline, acid and chelated kraft pulp leaching.

EQUIPMENT AND ANALYTICAL PROCEDURES

The industrial data and samples were collected under normal operational conditions and express the regular deviation observed in the mill fiber line. To evaluate each unit operation involved in the line, a stepwise survey was performed (Figure 1). The sampling period was extended through a month, with a sampling strategy that consisted in taking a complete set of samples every normal production day, at random hours of the day. Twenty sets of samples were collected, at the theoretical retention time for each sample in a set.

The Kappa numbers of the lab washed pulps were determined according to TAPPI T-236 method. The pH, conductivity, COD and colloidal counts were determined in the pulps filtrates. The conductivity, pH and COD analyses were performed according to Standard Methods for the Examination of Water and Wastewater. The colloidal count was performed by direct optical microscopy in a Neubauer counting chamber coupled to a CRT monitor. The lab trials were performed in a 20-Liter reactor to evaluate leaching and chelation of pulps. Testing conditions are described in the appropriate sections of this report for better clarity.

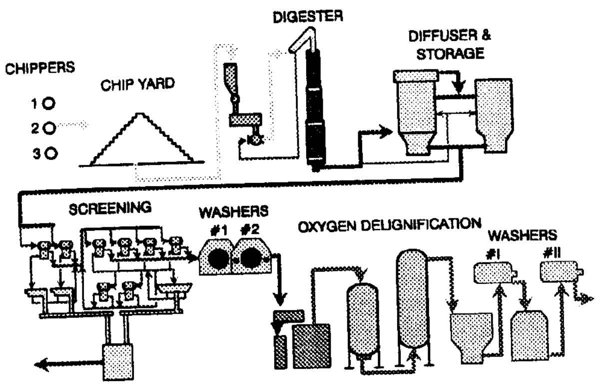

Figure 1 - Schematic description of Riocell's unbleached fiber line.

RESULTS AND DISCUSSION

Delignification Efficiency of the Fiber Line

The Kappa number technique is a standard method for delignification evaluation. It is not a direct determination of the lignin fragments and transformed molecular residues. The laboratory washing is also not correlated with the industrial handling of the pulp, which method gives no information about the washable portion of lignin that may migrate out the fibers during the laboratory manipulation of the sample. Previous studies have shown that prolonged washing of unbleached pulps enable lignin dissolution. References [3], [4], [5]. The dissolution increases with temperature, decreasing ionic strength and decreasing content of certain metal ions. The removal of lignin is controlled by the diffusion through the cell wall. Delignification during high temperature alkaline washing or post cooking has been of concern. Reference [6].

The first part of our work describes the behavior of lignin removal and filtrates quality along an unbleached kraft fiber line. Its production capacity is 1000 ADMT/day of eucalyptus pulp. In 1990 the mill started up an oxygen delignification plant in this line. Figure 2 describes the kappa number profile after each unit operation. The leaching of lignin is not an unexpected phenomena, and its extent and importance in our mill is valuable information.

Even before the operation of the oxygen reactor the mill reported some leaching across the unbleached washing line. This leaching effect was in the range of 1.5-2 units of kappa number after discharge of the digester. Figure 2 shows the increased leaching through all the unbleached fiber line. The range of kappa numbers handled in this line is as high as 19 at the digester discharge, decreasing to 7 after the delignification washer. No matter which statistical descriptive parameter is taken, there is a consistent profile of lignin removal. Potentially, 40% of the lignin in the pulp removed in these operations comes out prior to the oxygen reactor. The diffuser washer placed right after the digester and the last washing drum prior to the oxygen delignification reactor have the greatest influence on the lignin leaching in the reactor. One direct implication of such observations relates to the calculation of the delignification efficiency. This leaching effect in the washing equipment has increased since the oxygen delignification plant start-up. A calculation based on the in- and out-coming Kappa numbers of the reactor gives a 31% reduction. In the discussed case, any inclusion of one or more peripheral washing equipment in the balance gives a 40-47 % reduction. Such consideration brings up the discussion on how careful one must be in comparing distinct equipment and pulping lines. The installation of more than one reactor in series with its own washing system has determined a new kind of interference, with an increased result in the delignification effect. Such findings substantiate the modern trend of longer cooking times at lower temperature coupled double oxygen delignification systems.

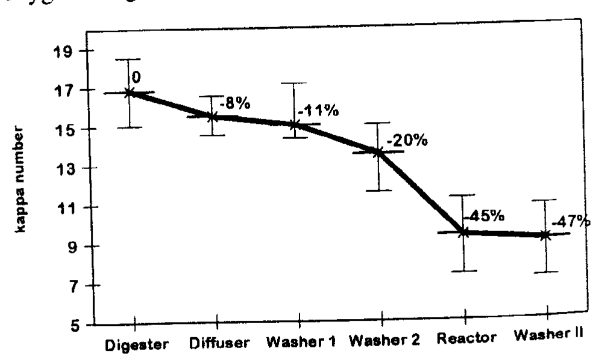

Figure 2 - Kappa number of the pulp between the kraft digester and the bleaching line. The percentages represent the delignification rate relatively to the analysis at the digester discharge. The vertical intervals relate to the max-min figures observed.

This work also aimed at describing the possible conditions that could explain the enhanced leaching. Figure 3 displays the COD of the pulp filtrates. It confirms that significant leaching has occurred. Such finding validates the use of Kappa number procedure to evaluate the system performance. Reference [7].

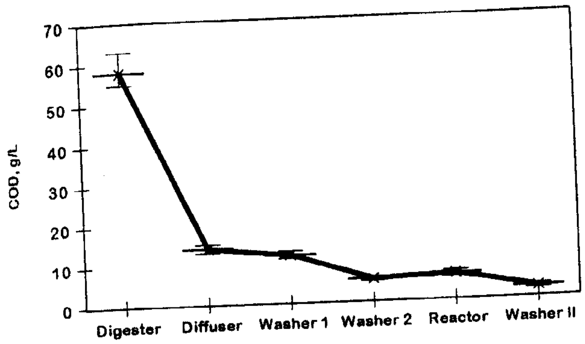

Figure 3 - COD concentration profiles in the filtrates from the pulp along the unbleached fiber line.

The pH and conductivity of filtrates were tested to confirm the alkalinity and conductivity hypotheses. Figure 4 provides the information that all the washing line before the oxygen reactor is operating near to 12 pH.

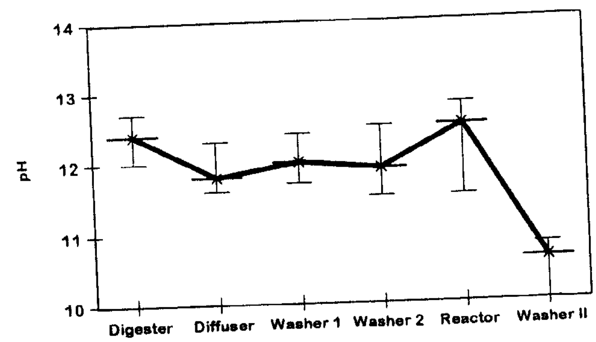

Figure 4 - pH profiles in the filtrates from the pulp along the unbleached fiber line.

Both the kraft digester and oxygen delignification reactor are operating at high pH values. High and constant alkalinity and prolonged time elapsed in the washing systems seem reasonable to explain leaching.

Conductivity measurements (not shown) were not so informative. A further speculation to explain the localized leaching is the counter-current recycling of washing filtrates. The impact of the oxidized filtrate from the oxygen delignification washing system (washers I and II), is not known. The conductivity measurements did not display any unusual profile. The washing positions where the pulp first contatcs oxidized filtrates from the oxygen reactor may cause near surface chemical changes on fibers. These changes could explain some minor leaching effects, but this has not been demonstrated yet.

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During the comissioning of the oxygen delignification plant in 1990, there were some short periods with the plant alternating the use of oxygen and alkali and only alkali at near nominal capacity. The effect of the alkali alone on the whole washing system could be evaluated. The typical results from selected 10 hour-periods of operation at each mode are summarized in Table I. These data confirm the off-reactor leaching that was discussed in Figure 2. The alkali charged at the reactor and the increase of temperature are accounting for c.a. 50% of the lignin leaching through the whole fiber line. One parallel question that arises from these considerations is how much of this leaching effect is part of the initial steep portion of the kinetic curve of the oxygen delignification.

Table I - Kappa number reduction based on digester discharge/oxygen reactor discharge in consecutive 10 hour-periods alternating supply of oxygen and alkali (regular operation) and only alkali (oxygen shutdown).

					Kappa Number		
reactor status	NaOH	O_2	Final temp.	pH in	digester	reactor	Δ diff.
	kg/ADMT	kg/ADMT	°C	-	-	-	%
with O_2	13.5	11	92	11.9	15.5	9.3	40
without O_2	10.6	0	87	11.7	15.5	11.7	25

Production: 930 ADMT/day

Colloidal Pitch Removal

One technical justification for our oxygen delignification plant was the effect it could bring in controlling pitch problems. The enhancement in washing and extractives oxidation were studied in our Technology Center and deemed to explain the better pitch control. The mill has been operating with a very low incidence of pitch problems after the startup of the oxygen delignification plant. The remaining pitch problems can be clearly associated to washing problems.

Figure 5 shows an extension of our conclusions about oxygen delignification benefits on pitch management. The colloidal dispersion is strongly influenced by the alkalinity profile established by the oxygen reactor. Alkalinity as a way for removing extractives is not a new issue, but a "second chance" to wash away the extractives using the reactor system certainly is very effective. A washing step has been doing a successful control of pitch problems in our mill.

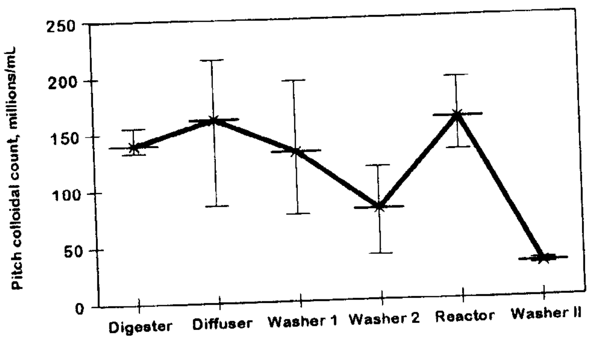


Figure 5 - Alkaline washing of colloidal pitch in the unbleached fiber line

LAB LEACHING STUDIES

A sample of pulp coming out of the last oxygen delignification washer (washer II) was tested in the lab for its leaching behavior. The aim was to establish the leaching potential after all industrial operations performed by the mill. Mild alkaline and acid conditions were used. For the alkaline treatments at 9 pH, an alkalinity similar to the pulp carry-over was used. For the acid treatments at 5 pH, both diluted sulphuric acid and acid filtrate from the bleaching plant were employed. The leaching stages were performed under atmospheric and pressurized conditions in a lab reactor. Table II summarizes the results.

This study has demonstrated that the leaching effect can be re-activated even after oxygen delignification and washing. This is not clear from the industrial data, shown in Figure 2. Leaching seemed to be minimum in the washing stage following the delignification reactor. Leaching was believed to occur only before the oxygen delignification stage at high alkali charge. Reference [6]. It was confirmed at our mill. After the delignification washing, alkaline leaching markedly decreases. Pressurized trials produced poor lignin removal, confirming industrial performance.

Table II - Laboratory studies on pulp leaching potential after industrial oxygen delignification and washing.

	Lab leaching stages : 8% consistency, 60 minutes					
	Atmospheric, 100°C			Pressurized, 120°C		
	sample (washer II)	alkaline	acid (H_2SO_4)	alkaline	acid (H_2SO_4)	acid filtrate
initial pH	9.0	9.0	5.0	9.0	5.0	5.0
kappa number	9.0	8.6	7.6	8.5	6.1	7.9
viscosity, cm^3/g	880	890	870	870	860	-
brightness, % ISO	51.1	54.5	54.4	54.6	54.2	54.0

Re-activation of leaching by mild acid treatment has proved successful. Both atmospheric and pressurized stages reduced the Kappa number. The pressurized trial is promising. A further reduction of the kappa number has resulted, without significant viscosity loss. Studies with acid filtrate washing from the bleaching plant were not as promising as with the pure acid addition. We are now investigating the chloride salt content (salting in/out effects) and chlorinated lignin micelles absorption as variables to explain such complex behavior. This portion of our research is in line with a recent published work dealing with water quality. Reference [7].

CHELATED KRAFT COOKING PRIOR TO OXYGEN DELIGNIFICATION

Chelation of pulp has been necessary to achieve brightness targets for TCF grades. We performed some preliminary tests doing lab chelated cookings and subsequent oxygen delignification.

The chelated cooking produced a pulp very similar to a regularly cooked pulp in our lab. The only important difference was the metals content. Table III displays a comparison of normal metal content and after chelation at similar cooking conditions.The amounts of metals are extremely low, except for the iron content. We know from previous studies that the iron is difficult to remove, due to its coordinated state in the fiber wall. This is a good option to simplify any future TCF bleaching line. The digester chelation enables the reduction of the number of chelating stages and seems very efficient.

Table III- Metals content of a pulp from eucalyptus wood cooked with and without chelant (1% DTPA, dry wood basis). Cooking conditions: 19.5% A.A., 8% Sulphidity, 0.018% AQ, to achieve Kappa 17.

	mg/kg OD pulp							
cooking	Ca	Mg	Mn	Fe	Cu	V	Co	Cr
Standard	948	153	21	20	2	<1	<1	traces
DTPA 1%	-	-	2	12	3	<1	<1	traces

The behavior of a chelated pulp in the oxygen delignification stages reduced the delignification activity, but enhanced somewhat the brightness and selectivity. To produce a lab delignification of 40% reduction in kappa number, two sucessive delignification steps were applied. Normally a single step is enough, as seen in Table IV.

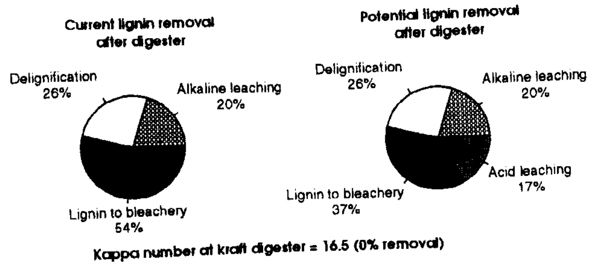
Table IV - Oxygen delignification of a standard pulp and a chelated pulp. 12% consistency, 95 °C, 45 minutes, 1,5% NaOH, 0.7 MPa O_2.

	Standard pulp		Chelated pulp
	single stage delignification	single stage delignification	double stage delignification
kappa number	10.1	11.7	10.4
viscosity, cm³/g	910	1040	960
brightness, % ISO	50.4	53.0	58.1

The decrease in delignification extent is in line with the proposed mechanism of oxygen delignification involving redox processes mediated by metal complexes. Reference [8]. The removal of almost all leachable metals slowed down the overall reaction, but has not stopped it. Reference [9]. Manganese is reported to be a catalyst for delignification, but its highly colored precipitates hinders practical use. Its removal from the pulp may explain slower delignification and higher brightness and viscosities achieved. This strategy of digester chelation helps the metals management, with respect to controlled use of catalysts and promoters.

CONCLUSIONS

The mill investigation has demonstrated how important the leaching effect is. The lab investigation has identified a promising approach in the concept of acid leaching. The pressurized condition and controlled water quality are important parameters to study.



Metals management is a tricky question. On one hand, the lab trials have demonstrated that the digester chelation is very effective. On the other hand, early chelation interferes with the reaction kinetics of delignification. Much more work is needed on this subject, because of the perceived potential it has.

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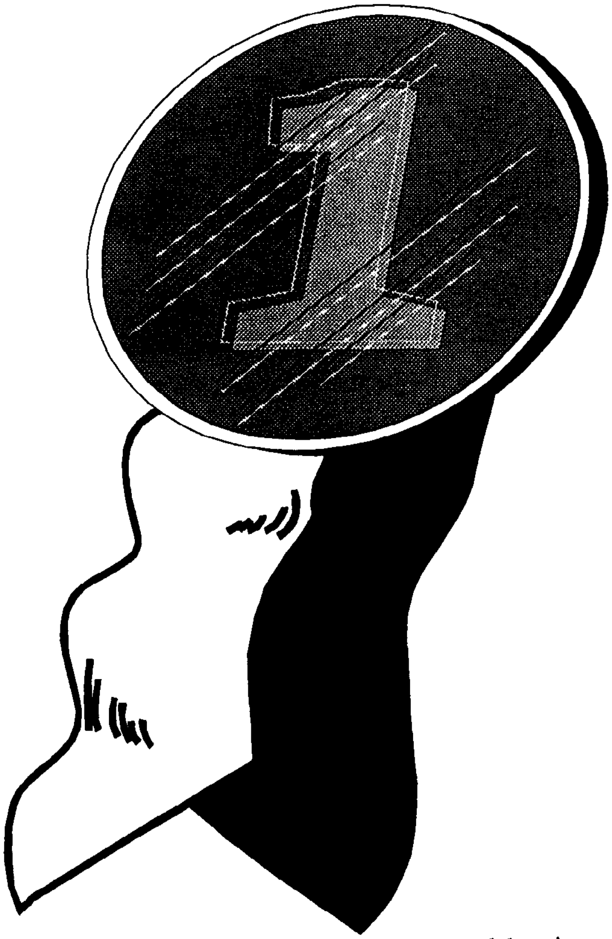

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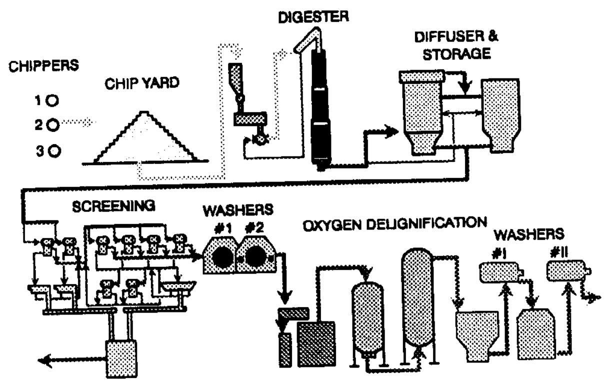

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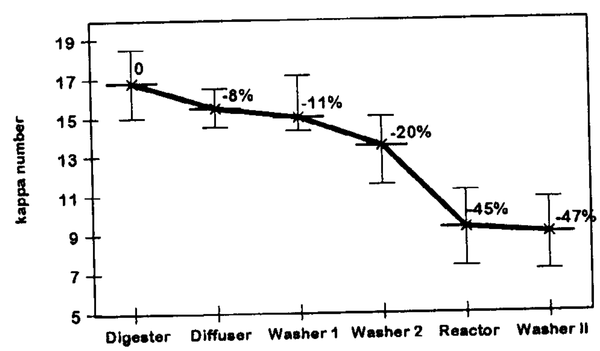

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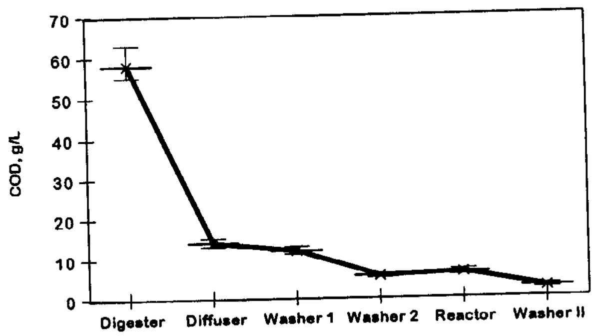

Figure 3 - COD concentration profiles in the filtrates from the pulp along the unbleached fiber line.

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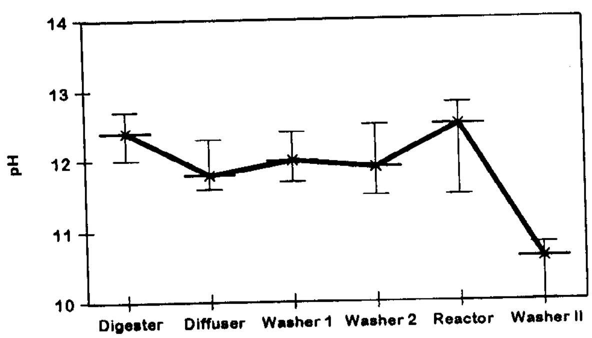

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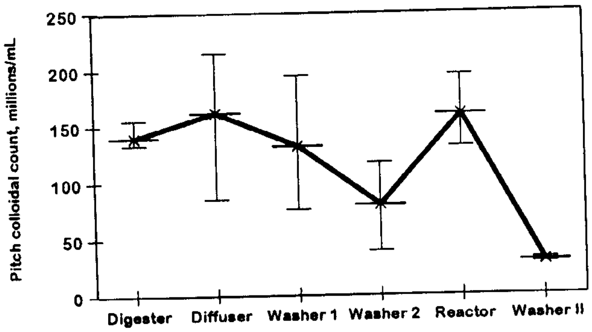

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This study has demonstrated that the leaching effect can be re-activated even after oxygen delignification and washing. This is not clear from the industrial data, shown in Figure 2. Leaching seemed to be minimum in the washing stage following the delignification reactor. Leaching was believed to occur only before the oxygen delignification stage at high alkali charge. Reference [6]. It was confirmed at our mill. After the delignification washing, alkaline leaching markedly decreases. Pressurized trials produced poor lignin removal, confirming industrial performance.

Table II - Laboratory studies on pulp leaching potential after industrial oxygen delignification and washing.

	Lab leaching stages : 8% consistency, 60 minutes					
		Atmospheric, 100°C		Pressurized, 120°C		
	sample (washer II)	alkaline	acid (H_2SO_4)	alkaline	acid (H_2SO_4)	acid filtrate
initial pH	9.0	9.0	5.0	9.0	5.0	5.0
kappa number	9.0	8.6	7.6	8.5	6.1	7.9
viscosity, cm^3/g	880	890	870	870	860	-
brightness, % ISO	51.1	54.5	54.4	54.6	54.2	54.0

Re-activation of leaching by mild acid treatment has proved successful. Both atmospheric and pressurized stages reduced the Kappa number. The pressurized trial is promising. A further reduction of the kappa number has resulted, without significant viscosity loss. Studies with acid filtrate washing from the bleaching plant were not as promising as with the pure acid addition. We are now investigating the chloride salt content (salting in/out effects) and chlorinated lignin micelles absorption as variables to explain such complex behavior. This portion of our research is in line with a recent published work dealing with water quality. Reference [7].

CHELATED KRAFT COOKING PRIOR TO OXYGEN DELIGNIFICATION

Chelation of pulp has been necessary to achieve brightness targets for TCF grades. We performed some preliminary tests doing lab chelated cookings and subsequent oxygen delignification.

The chelated cooking produced a pulp very similar to a regularly cooked pulp in our lab. The only important difference was the metals content. Table III displays a comparison of normal metal content and after chelation at similar cooking conditions.The amounts of metals are extremely low, except for the iron content. We know from previous studies that the iron is difficult to remove, due to its coordinated state in the fiber wall. This is a good option to simplify any future TCF bleaching line. The digester chelation enables the reduction of the number of chelating stages and seems very efficient.

Table III- Metals content of a pulp from eucalyptus wood cooked with and without chelant (1% DTPA, dry wood basis). Cooking conditions: 19.5% A.A., 8% Sulphidity, 0.018% AQ, to achieve Kappa 17.

	mg/kg OD pulp							
cooking	Ca	Mg	Mn	Fe	Cu	V	Co	Cr
Standard	948	153	21	20	2	<1	<1	traces
DTPA 1%	-	-	2	12	3	<1	<1	traces

The behavior of a chelated pulp in the oxygen delignification stages reduced the delignification activity, but enhanced somewhat the brightness and selectivity. To produce a lab delignification of 40% reduction in kappa number, two sucessive delignification steps were applied. Normally a single step is enough, as seen in Table IV.

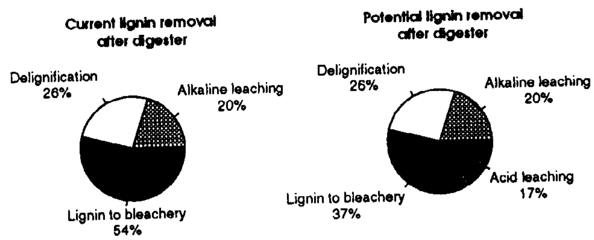
Table IV - Oxygen delignification of a standard pulp and a chelated pulp. 12% consistency, 95 °C, 45 minutes, 1,5% NaOH, 0.7 MPa O_2.

	Standard pulp		Chelated pulp
	single stage delignification	single stage delignification	double stage delignification
kappa number	10.1	11.7	10.4
viscosity, cm^3/g	910	1040	960
brightness, % ISO	50.4	53.0	58.1

The decrease in delignification extent is in line with the proposed mechanism of oxygen delignification involving redox processes mediated by metal complexes. Reference [8]. The removal of almost all leachable metals slowed down the overall reaction, but has not stopped it. Reference [9]. Manganese is reported to be a catalyst for delignification, but its highly colored precipitates hinders practical use. Its removal from the pulp may explain slower delignification and higher brightness and viscosities achieved. This strategy of digester chelation helps the metals management, with respect to controlled use of catalysts and promoters.

CONCLUSIONS

The mill investigation has demonstrated how important the leaching effect is. The lab investigation has identified a promising approach in the concept of acid leaching. The pressurized condition and controlled water quality are important parameters to study.



Kappa number at kraft digester = 16.5 (0% removal)

Metals management is a tricky question. On one hand, the lab trials have demonstrated that the digester chelation is very effective. On the other hand, early chelation interferes with the reaction kinetics of delignification. Much more work is needed on this subject, because of the perceived potential it has.

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Thursday, October 5
3:30 p.m.
AIChE Session 4

Chicago Ballroom VI

Oxygen Delignification

Session Co-Chairmen
P. W. Hart
Westvaco Corporation

A. W. Rudie
Inst. of Paper Science & Technology

3:30 p.m. Stepwise Survey on Oxygen Delignification and Pulp Washing Performance

E. Ratnieks, C. Foelkel, V. Sacon, and C. Zimmer
Riocell SA

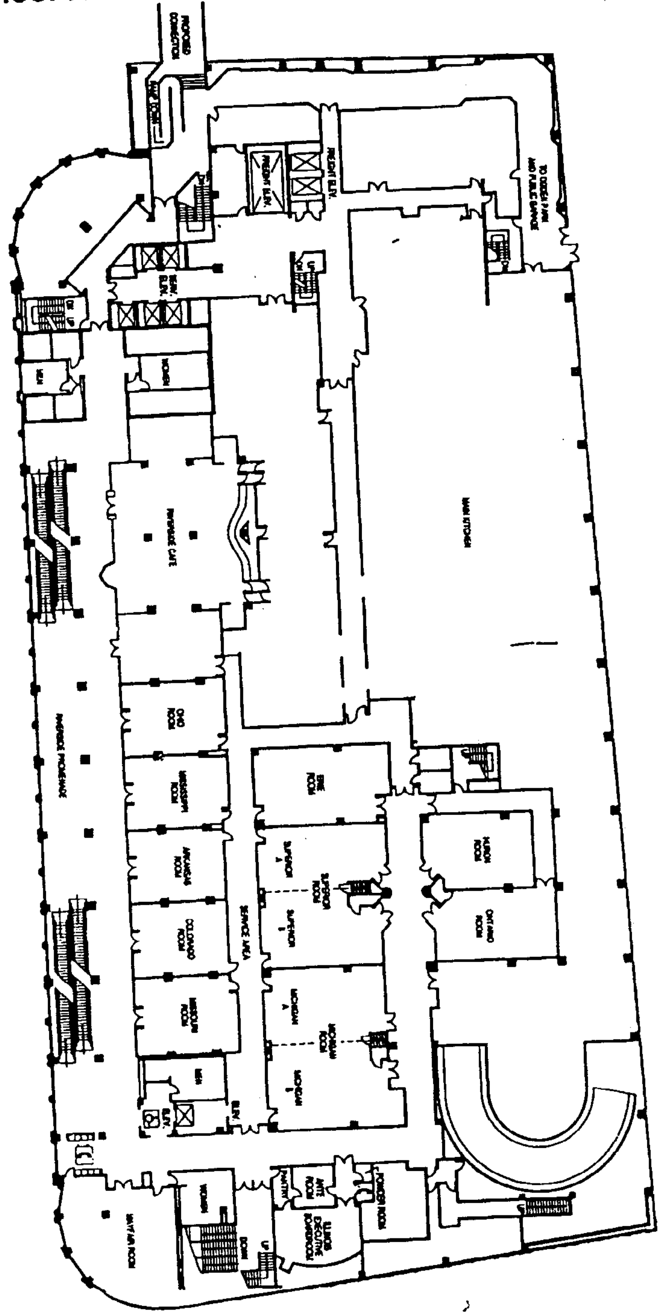
4:00 p.m. Oxygen Delignification of Southern Hardwoods

J. M. Genco and E. Guven
University of Maine

4:30 p.m. Oxygen Delignification: Evaluation of Process Variables

D. Sorenson, D. Carter, A. Johnson, and D. McKenzie
Simons Engineering

Floor Plans - Level 2



›nference Events

ırday, September 30		Room/Floor
a.m.	International Pulp Bleaching Prog. Cmte. Mtg.	Missouri/2
a.m.	Leadership Workshop	Ohio/2
day, October 1		
a.m.	*Pulp Bleaching Steering Cmte	Ohio/2
a.m.	Mill Closure Subcmte	Missouri/2
a.m.	Bleach Plant Operations Subcmte	Mississippi/2
a.m.	*Pulp Manufacture Division Council	Parlor C/3
) a.m.	Oxygen, Ozone & Enzyme Subcmte	Huron/2
) a.m.	Chemical & Mechanical Pulp Bleaching Subcmte	Ontario/2
ı	*TAPPI President's Representative Luncheon	Mayfair/2
	Registration Opens	Convention Registration/3
p.m.	Speaker Ready Room	Arkansas/2
p.m.	Alkaline Pulping Steering Subcmte	Superior B/2
p.m.	Pulp Bleaching Cmte	Sheraton Ballroom V/4
p.m.	Nonwood Plant Fibers Cmte	Missouri/2
p.m.	Technical Program Orientation	Michigan A&B/2
p.m.	Speaker Ready Room Closes	Arkansas/2
p.m.	*Conference Chairman's Reception	Sheraton Ballroom I/4
p.m.	Registration Closes	Convention Registration/3
day, October 2		
ı.m.	*Speakers' & Session Chairmen Breakfast (Slide Preview Center)	Michigan A&B/2
ı.m.	Registration Opens	Convention Registration/3
ı.m.	Guest Hospitality Breakfast	Spectators Bar/3
ı.m.	*VIP Continental Breakfast	Parlor A/3
ı.m.	Opening Keynote Session	Chicago Ballrooms VI & VII/4
a.m.	Break	Chicago Ballrooms VIII/IX/X/4
a.m.	Poster Session Opens	Chicago Ballrooms VIII/IX/X/4
a.m.	Session 1: AQ-PS Pulping	Sheraton Ballroom III/4
m.	Session 2: TCF Bleaching	Sheraton Ballroom V/4
a.m.	Session 3: Straw & Grass Pulping	Missouri/2
a.m.	Session 4: Contaminants & OCC	Sheraton Ballroom IV/4
m.	Supplier Cmte	Ohio/2
m.	Session 5: Process Control	Sheraton Ballroom III/4
m.	Session 6: Bleaching Tech I	Sheraton Ballroom V/4
m.	Session 7: Deinking Technology	Sheraton Ballroom IV/4
m.	Panel 1: 25th Anniversary of Nonwood	Missouri/2
m.	Panel 12: Turpentine Safety	Chicago Ballroom VI/4
m.	Break	Chicago Ballrooms VIII/IX/X/4
m.	Panel 2: Pulp Quality	Sheraton Ballroom III/4
m.	Panel 3: Ozone Generation	Sheraton Ballroom V/4
m.	Panel 4: Recycling Wax Coated Cartons	Sheraton Ballroom IV/4
m.	Poster Session Closes	Chicago Ballrooms VIII/IX/X/4
m.	Pulp Washing 96 Technical Program Cmte	Parlor F/3
m.	Conference Reception	Chicago Ballrooms/VI-X/4
m.	Registration Closes	Convention Registration/3

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TAPPI PROGRAM

1995 TAPPI Pulping Conference

October 1-5
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TAPPI
Technology Park/Atlanta
P.O. Box 105113
Atlanta, GA 30348-5113 USA
Service Line 800-332-8686
Telephone (770) 446-1400
FAX (770) 446-6947