Commercial TCF Bleach Plant Design and Effect of Solids and Thermal Balance on Operations

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Abstract

The major expansion of any pulp mill facility today must consider the future market demands for products as well as regulations for the outfall from the pulp mill. Even today, the supply of pulp and paper products into some European countries demands minimal use of chlorine compounds in the bleaching or the total elimination of the use of chlorine in the bleach plant. It is best then to design modern facilities without the use of chlorine but maintaining pulp and paper quality comparable to current standards based on conventional chlorine based technology.

In order to design a fiberline to meet these criteria, it is necessary to consider not only the bleaching response and pulp quality, but the impact on the mill infrastructure when implementing new technology. Today, a market pulp produced from Brazilian eucalyptus must be bleached to a minimum 88% ISO reverted (90+% ISO bleached).

This study includes laboratory analysis to define a desirable TCF bleaching sequence, and assesses the impact on the infrastructure of the mill regarding water use, effluent flow, and impact on recovery including the sodium/sulfur balance. The results of this work are compared to a conventional chlorine based bleaching sequence, and a new ECF sequence is identified which may be attractive as an interim step towards the closed cycle mill.

Introduction

A laboratory study was performed to evaluate potential non-chlorine bleaching sequences. Based on prior work, it was clear that it would be necessary to use an oxidant other than just oxygen and hydrogen peroxide since the use of only these chemicals cannot produce high quality 90+%ISO brightness eucalyptus pulp. The use of ozone gas for bleaching pulp is becoming well established and is currently used in several bleach plants in Scandinavia and Europe(1) for production of fully bleached hardwood and softwood, kraft and sulfite pulps. In addition, it is used in the United States to produce a bleached ECF pulp for integrated use for manufacture of fine papers.(2)

It is well established that eliminating chlorine and chlorine dioxide from the bleaching sequence requires a low kappa number entering the bleach plant in order to achieve high brightness with high pulp quality. A kappa number from 12-14, or below, to the oxygen stage was expected to be required. Typical kappa in a conventional chlorine based bleach plant for eucalyptus is 17-18. It was decided that the most versatile fiberline design for

producing TCF pulps would be one which included extended delignification. The pulp produced for this study was an extended delignified batch cooked pulp (by the RDH process) which had and unbleached kappa of 11.6 and a viscosity of 44.1 cps.
The overall bleach plant configuration and its expected capital and operating cost characteristics was considered in the design of the laboratory study.

Establishment of the Bleaching Sequence

The simplest bleach plant using oxygen, ozone and peroxide is the OZP sequence, which was first evaluated for production of fully bleached eucalyptus pulp. Data from the bleaching of this pulp based on the initial OZP sequence is shown in Table 1

At moderate levels of ozone and peroxide (0.4% and 1.0%, respectively), this sequence achieved a brightness of 84.4%ISO at a viscosity of 12.6 cps. Based on previous work, it was not expected that increased use of ozone and peroxide alone in this short sequence would be successful in achieving the target 90+%ISO brightness at acceptable pulp strength, so additional bleaching stages were evaluated.

Table 1: Evaluation of OZP Based Sequences

Stage	Chemical (%)	Consistency (%)	Kappa	Viscosity (cps)	Brightness (% ISO)	Rev.Br. (%ISO)
Unbleached	n/a	nm	11.6	44.1	36.2	nm
Oxygen (O)	1.6	nm	nm	28.2	56.3	nm
Ozone (Z)	0.4	0.4	2.1	18.3	70.2	nm
Peroxide (P)	1.5	1.0	–	12.6	84.4	nm
OZP (0.4%Z)	–	–	–	**12.6**	**84.4**	**nm**
Ozone (Z2)	0.08	0.08	nm	11.2	88.8	86.4
OZPZ	–	–	–	**11.2**	**88.8**	**86.4**
Ozone (Z2)	0.16	0.16	nm	10.5	89.7	86.8
OZPZ	–	–	–	**10.5**	**89.7**	**86.8**
Ozone (Z2)	0.3	0.3	nm	10.4	90.2	86.7
OZPZ	–	–	–	**10.4**	**90.2**	**86.7**
Ozone (Z2)	0.16	0.16	–	10.5	89.7	86.8
FAS (FAS)	1.0	nm	nm	9.8	89.6	88.5
OZPZFAS	–	–	–	**9.8**	**89.6**	**88.5**
ClO2 (D)	0.5	0.5	nm	12.4	90.2	88.1
OZPD	–	–	–	**12.4**	**90.2**	**88.1**

Since the pulp produced with the OZP sequence was evidently a very low kappa number and was very bright (84.4%ISO), the use of a small amount of chlorine dioxide (0.5%) was capable of meeting the target brightness and had a viscosity of 12.4 cps. This sequence is likely to be optimized to use significantly less chlorine dioxide, but since it is an ECF rather that the desired TCF sequence, it was not pursued further.

Since it is clear that ozone is not only a powerful delignification agent but also a powerful brightening agent, the addition of a second stage of ozone in the final bleaching stage was considered to be attractive, especially since it is necessary for the pulp to enter the pulp machine on the acid side. Several doses of ozone were applied at the end of the sequence and the target bleached brightness was achieved using a total ozone charge of 0.7% and a total peroxide consumption of 1.0%. However, with the ozone stage at the end of the sequence, the pulp exhibited significant reversion (3.5%ISO).

In order to stabilize the brightness, a final stage of FAS (formadine acid sulfimic) was applied to the pulp, which resulted in a reduction of the reversion to 1.1%ISO, or a pulp which met the target 88+%ISO reverted brightness, at a viscosity of 9.8. As FAS is a rather expensive chemical to use on a commercial scale for bleaching, and since this sequence would require a full additional stage of bleaching requiring additional capital cost, it was determined that this sequence was not attractive for commercial use.

Summary of OZP Based Sequences:

1. The OZPZ sequence is capable of very high brightness (>88%ISO) while maintaining a viscosity of greater than 10 cps. At the target 90%ISO brightness, a viscosity of 10.4 cps is achieved with the use of 0.7% ozone and 1.0% peroxide (consumed).
2. The pulp exhibited significant reversion when ozone is used as the final bleaching stage. Reversion of 3.5%ISO is exhibited at a bleached brightness of greater than 90%ISO.
3. The use of 1.0% FAS (formadine acid sulfimic) added to the OZPZ bleached pulp is capable of reducing the level of reversion from 3.5 %ISO to 1.1%ISO.
4. The OZP bleached pulp has a brightness of 84.4%ISO and a viscosity of 12.6 cps, and can be treated in a mild final chlorine dioxide stage (0.5% on pulp) to meet the target 90+%ISO (88+%ISO reverted) with a viscosity of 12.4 cps.

In order to increase the power of the bleaching sequence, the addition of an oxidative extraction stage following the ozone stage was known to be a cost effective approach. From previous work on eucalyptus pulp, the addition of Eo to an OZP sequence (to an OZEoP sequence) generally results in an increase in brightness of 1.5-2 %ISO with a simultaneous increase in viscosity. As this change alone is not sufficient to achieve the targets for this pulp, the pulp was treated also with a mild second ozone bleaching stage in an OZEoZP sequence.The OZEoZP sequence has been proposed as a very powerful bleaching sequence with great potential to produce fully bleached high brightness pulps.(3,4) The bleaching results from this sequence are shown in Table 2.

With the use of a little more than 0.4% ozone on pulp, the OZEoZP sequence achieved the target bleached and reverted brightnesses of 90+%ISO and 88+%ISO, respectively.

Summary of the OZEoZP Sequence:

1. The OZEoZP sequence is capable of very high brightness (92+%ISO) while maintaining viscosity of 7.8 cps. At the target 90%ISO brightness, a viscosity of over 8 cps is to be expected with the use of 0.45% ozone and 1.5% peroxide (consumed).
2. The brightness stability of the TCF bleach plant with peroxide as the final stage, the brightness stability is very good, with reversion of 1.8 - 2.2 %ISO at bleached brightness of greater than 90%ISO.

Table 2: Evaluation of the OZEoZP Sequence

Stage	Chemical (%)	Consistency (%)	Kappa	Viscosity (cps)	Brightness (% ISO)	Rev.Br. (%ISO)
Unbleached	n/a	nm	11.6	44.1	36.2	nm
Oxygen (O)	1.6	nm	nm	28.2	56.3	nm
Ozone(Z1)	0.4	0.4	2.1	18.3	70.2	nm
Extraction (Eo)	1.2	nm	1.3	14.5	77.5	nm
OZEo (0.4%Z)	--	--	**1.3**	**14.5**	**77.5**	nm
Ozone (Z2)	0.13	0.13	nm	17.4	85.0	nm
Peroxide (P)	2.0	1.8	nm	6.9	91.5	89.7
OZEoZP	--	--	--	**6.9**	**91.5**	**89.7**
Ozone (Z2)	0.2	0.2	nm	10.3	85.3	nm
Peroxide (P)	2.0	1.5	nm	7.8	92.2	90.2
OZEoZP	--	--	--	**7.8**	**92.2**	**90.2**
Unbleached	n/a	nm	11.6	44.1	36.2	nm
Oxygen (O)	1.6	nm	nm	28.2	56.3	nm
Ozone(Z1)	0.2	0.2	3.0	19.2	64.7	nm
OZEo (0.2%Z)	--	--	3.0	19.2	64.7	nm
Ozone (Z2)	0.2	0.2	1.2	13.6	78.1	nm
Peroxide (P)	2.0	1.5	nm	8.5	89.4	86.8
OZEoZP	--	--	--	**8.5**	**89.4**	**86.8**
Ozone (Z2)	0.3	0.3	1.2	11.5	80.9	nm
Peroxide (P)	2.0	1.2	nm	7.1	91.9	89.7
OZEoZP	--	--	--	**7.1**	**91.9**	**89.7**

Strength of TCF bleached pulps

Throughout the course of the bleaching evaluation, the viscosity of the pulp was monitored as an indicator of potential pulp strength. It is known, however, that the absolute viscosity of pulps bleached in ECF or TCF sequences using ozone cannot be compared to the viscosity of conventional chlorine based bleach sequences. The bleaching of pulp using ozone introduces on the pulp a large fraction of carbonyl end groups which are quite sensitive to cleavage in a highly alkaline medium. This highly alkaline medium is encountered in the test procedure for viscosity, so the ozone bleached pulps will exhibit an "apparent" low viscosity, even though the pulp strength is not affected. This effect has been studied extensively and published several times over the last several years. Apparently, the original work describing this effect is by Godsey.(5) In this work, Godsey describes the stabilization after the ozone treatment of the carbonyl end groups with sodium borohydride. Subsequent bleaching is not affected by this stabilization step, but the "apparent" viscosity of the final bleached pulp is significantly higher. Unfortunately, since absolute viscosity is still accepted by many in the industry as an important parameter, some laboratories and researchers are using this method to create viscosity readings on ozone bleached pulps which seem more palatable to pulp producers. It is therefore quite important to understand the technique for laboratory pulp bleaching and viscosity determination during evaluation of laboratory data.

Even though the viscosity of the ozone bleached pulp does not by itself indicate pulp strength, changes in viscosity, as with conventionally bleached pulps, indicate the potential for a stronger or weaker pulp. In other words, at the same level of pulp strength, the ozone bleached pulps will exhibit lower viscosity. A comparison of ECF and TCF pulp viscosity at equivalent strength is shown on Table 3.

In order to evaluate bleaching sequences for commercial implementation, it is critical to evaluate the strength of the pulps. In numerous TCF bleaching sequences using ozone and peroxide on this eucalyptus pulp, the strength of the pulp was found to be comparable to the conventional chlorine based bleached pulp produced in the laboratory and commercially. Laboratory beater analysis data are shown in Table 4 and 5. The data in Table 5 represent the average of TCF bleached pulps which were found to meet the target criteria.

Figures 1 - 5 show the properties of the TCF pulps compared to the conventional chlorine based bleaching sequence ODEoD. The TCF pulps exhibit strength properties which are equal or within 10% of the reference.

Table 3: Strength Properties of TCF Eucalyptus Pulps

	ECF	TCF
Brightness, % ISO	90.8	90.8
Viscosity, cm^3/g	900	550
Viscosity, cP	20	9
Post-color number	0,60	0,28

Table 4 : Strength Properties of ECF Pulp

PFI Revolutions	0	500	1300	3500	7200
°Schopper Riegler	21	25	30	40	55
CSF, ml	530	470	410	290	175
Tensile, N.m/g	46.4	62.1	80.6	104.3	113.3
Stretch, %	2.5	3.1	3.8	4.7	4.8
Burst, $kPa.m^2/g$	2.2	3.3	4.8	7.4	9.2
Tear, $mN.m^2/g$	8.4	11.2	12.9	12.7	11.6
Bulk, cm^3/g	1.91	1.78	1.63	1.47	1.34
Air Resistance, $s/100cm^3$	2.0	4.5	9.1	35.4	123.4
Printing opacity, %	79.7	78.7	77.4	74.5	70.7
Brightness, %ISO	90.5	89.4	89.1	88.2	87.6
Klemm water absorption, mm/10 min	82	68	53	32	19

Table 5: Strength Properties of TCF Pulp

PFI Revolutions	0	200	900	3000	5700
°Schopper Riegler	22	25	30	40	55
CSF, ml	510	470	410	290	175
Tensile, N.m/g	45.2	53.2	67.5	93.8	105.5
Stretch, %	2.6	3.2	3.8	4.6	5.1
Burst, $kPa.m^2/g$	1.9	2.6	3.8	6.1	7.8
Tear, $mN.m^2/g$	8.3	11.0	11.9	12.5	11.9
Bulk, cm^3/g	1.86	1.78	1.65	1.49	1.42
Air Resistance, $s/100cm^3$	1.4	2.4	5.8	18.9	67.7
Printing opacity, %	78.6	78.1	76.7	74.6	73.7
Brightness, %ISO	90.5	89.8	89.5	88.6	87.7
Klemm water absorption, mm/10 min	84	73	56	36	23

Figure 1: Tensile vs. Tear for ECF and TCF Pulps

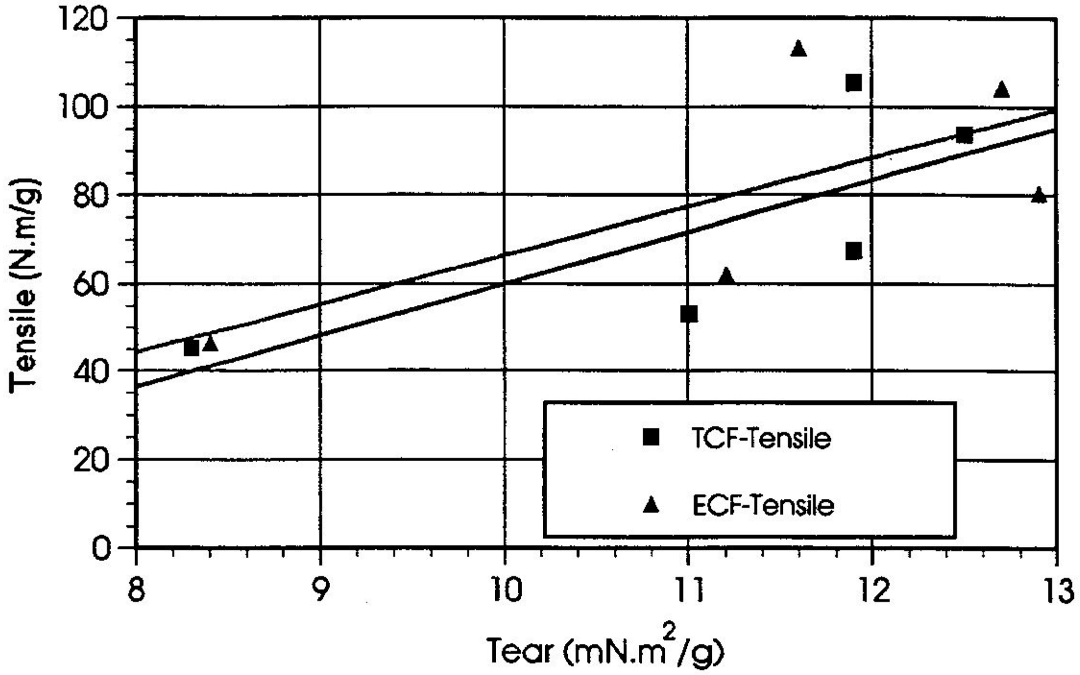


Figure 2: Tensile and Bulk vs Freeness for ECF and TCF Pulps

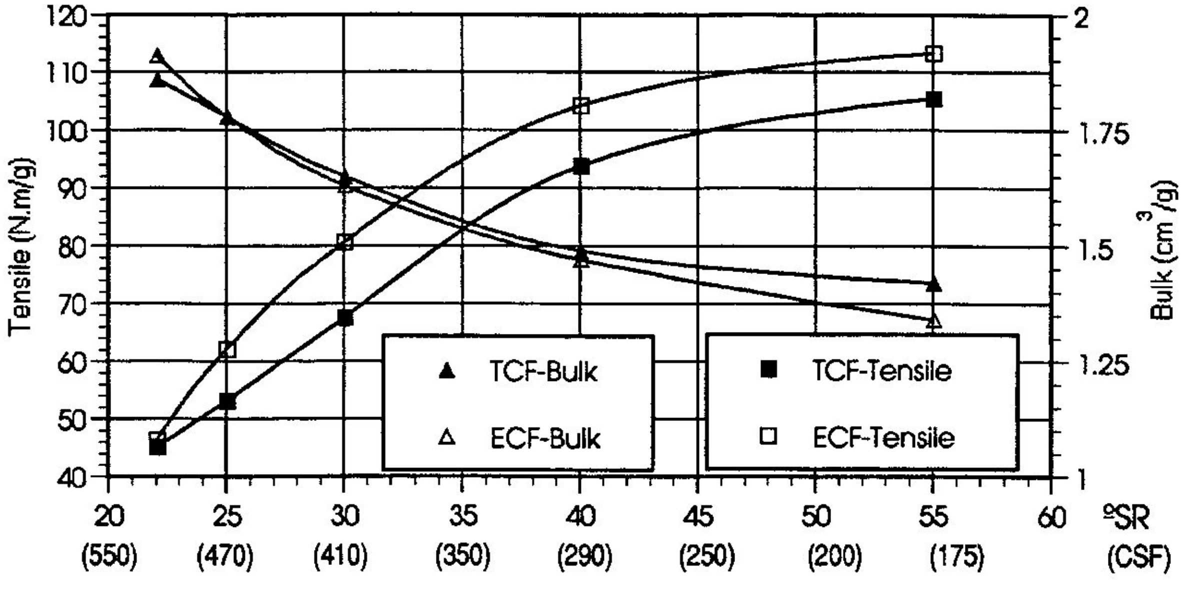


Figure 3: Tear and Printing Opacity vs. Freeness for ECF andTCF Pulps

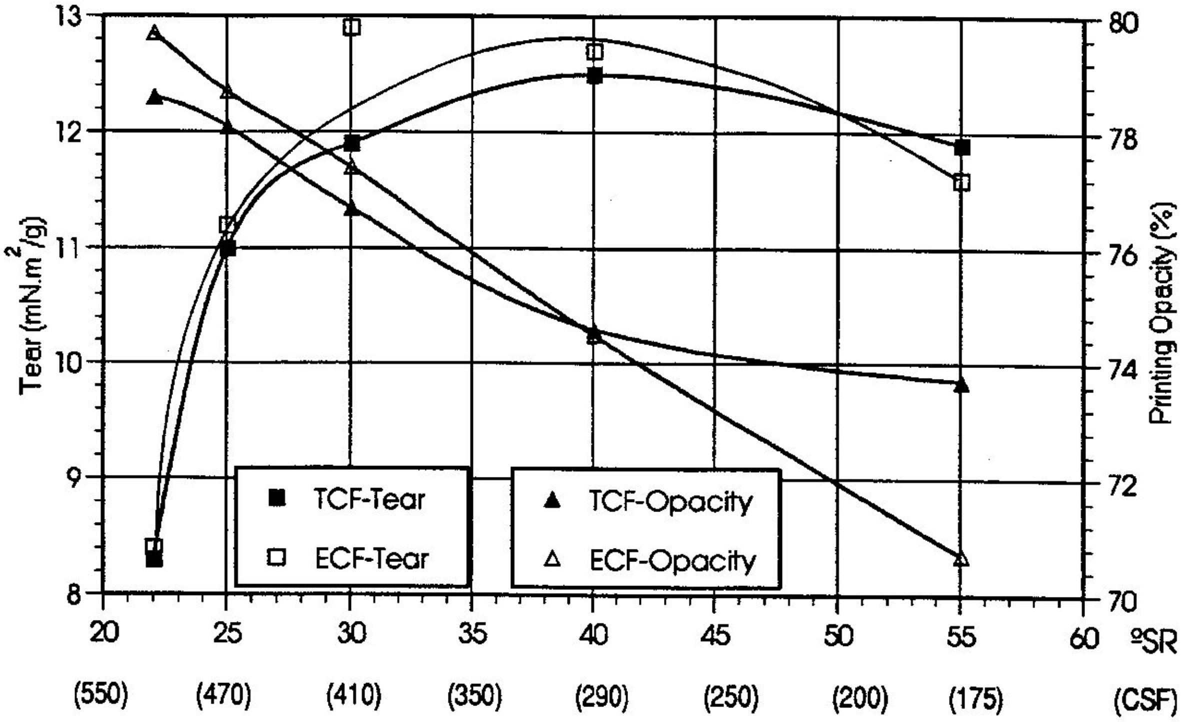


Figure 4: Burst and Klemm Water Absorption vs. Freeness for ECF and TCF Pulps

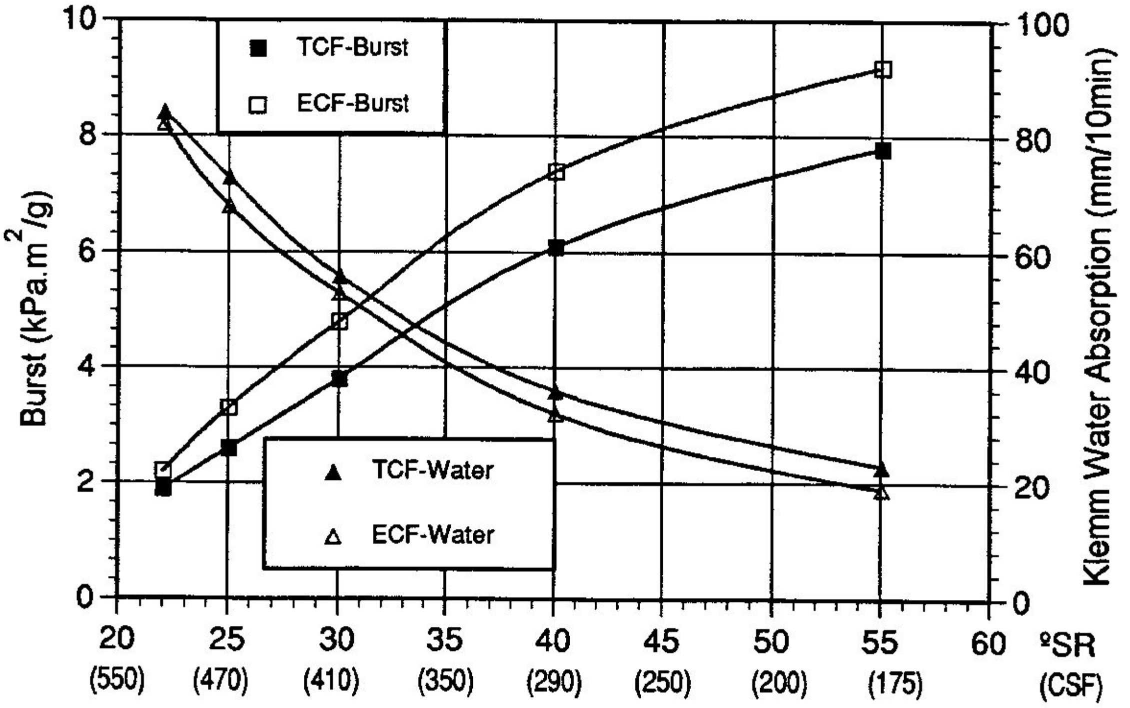
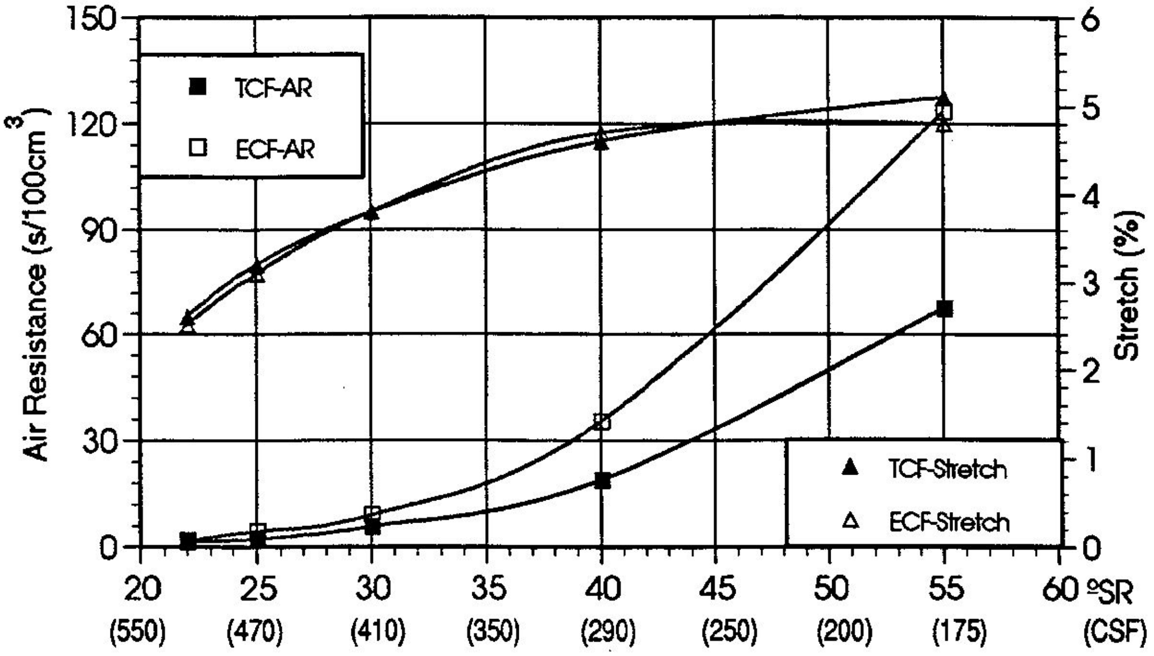


Figure 5: Air Resistance and Stretch vs. Freeness for ECF and TCF Pulps



Integration into System

The OZEoZP sequence can be implemented into commercial operation using either medium or high consistency ozone and peroxide stages. For purposes of this study, we have assumed a bleaching plant operating at 1200 madtpd. The ultimate selection depends on a detailed economic analysis of capital and operating cost for a given installation.

As is well known, the medium consistency ozone stage is limited in the amount of ozone which may be contacted with the pulp due to a limit of the volume ratio of gas to pulp.(6,7) In addition, it is more sensitive to carryover of solids to the stage than high consistency.(8) As the ozone application in and the solids carryover to the second ozone stage is quite low, the second ozone stage is considered only as a medium consistency stage. The first stage of ozone may be high or medium consistency. For this evaluation, only high consistency ozone in the first stage is considered. The evaluation of high or medium consistency peroxide is beyond the scope of this paper, so it is assumed that for purposes of this analysis, the peroxide stage is operated as a medium consistency stage.

The bleach plant can be constructed with or without washing of the pulp between the ozone and oxidative extraction stages. The choices then become the following, where "Zh" represents high consistency ozone and "Zm" represents medium consistency ozone:

1. ZhEoZmP
2. (ZhEo)ZmP

In order to evaluate the total bleach chemical cost for the various options, it is necessary to estimate the use of acid and alkali, as well as the impact of solids carryover in the system.

Acid and Alkali Use

It is difficult to predict acid and alkali use in the bleach plant from laboratory evaluations and computer simulations. This estimate has been performed by using titration data on commercially produced pulps. It was assumed that the acids and alkalis contained in the pulp slurries at various pH levels were ideal and completely dissociated. This allowed a base case to be established among the options to be considered. The data was then adjusted based on empirical data from early operation of commercial ozone bleaching stages, which as a net result increased the acid consumptions by about 40-50%. The results are as follows:

Table 6: Acid and Alkali Consumption

Sequence	Acid (H_2SO_4) (kg/t)	Alkali (NaOH) (kg/t)
ZhEoZP	12.4	10.0
(ZhEo)ZP	19.4	11.4

The lowest use of acid and alkali is achieved with the ZhEoZP sequence as expected. It is noted, however, that there is not a large difference in the acid and alkali use whether there is or is not washing between the Zh and Eo stages. Recent data on a similar eucalyptus pulp indicated no significant difference in brightness response, although it was necessary to use additional NaOH/t for the Eo stage when there is no washing between stages. Quantitatively, the elimination of the Zh washer results in an increased acid use of 7 kg/t and an increased alkali use of 1.4 kg/t. At a 1200 madtpd pulp mill, with an acid cost of US$50/t and alkali cost of US$300/t, this results in an operating cost penalty of less than US$350,000/year. This savings alone does not justify the installation of a Zh washer.

The total bleach chemical use for the OZEoZP sequence is shown on Table 7.

Impact of Solids Buildup

Where TCF bleach plants are designed to recover most or all of the solids from the bleaching, it is necessary to purge metals from the system to minimize the use of ozone and peroxide in the bleach plant. Transition metal ions are known to dramatically affect the efficiency of peroxide stages, and to a lesser extent, the ozone bleaching stage. A strong acid wash is very efficient at removing metal ions from the pulp, and this can be supplemented with chelants if necessary in a particular installation. As the ozone bleaching stage is optimized at a pH of 2.0 to 3.0, a strong acid wash is inherent in the design of a bleach plant using high consistency ozone as the first stage. In most cases, this eliminates the need for a subsequent chelant (Q) stage for removal of metals prior to the peroxide stage in the bleach plant. In order that detrimental metal ions are not reintroduced into the bleach plant downstream of the acid wash, all process streams entering the bleach plant must be evaluated for metal ions such as manganese, copper, iron, and cobalt.

Table 7: Bleach Chemical Use in O(ZEo)ZP Sequence

Bleach Chemical	**Sub-total (kg/madt)**	**Total (kg/madt)**
Oxygen		
O stage	16.0	
Eo stage	5.0	
Total		21.0
Ozone		
Z1 for delignification	3.0	
Z1 for COD carryover	1.2	
Z2 for delignification	1.5	
Z2 for COD carryover	0.8	
Total		6.5
Acid (H_2SO_4)		12
Alkali (NaOH)		
Eo	11.4	
H_2O_2	7.5	
Total		18.9
Peroxide (H_2O_2)		15.0

The amount of liquor which must be purged from the system to remove detrimental metal ions is in the range of 1 to 3 cubic meters per tonne pulp.(9) The balance of the filtrate is recirculated to recovery. In this configuration, the solids level entering the ozone stage rises due to this recirculation. Simulation data for the two configurations result is as follows:

Table 8: Solids Buildup (kg total dissolved solids/madt)

Purge Rate (m3/madt)	**0**	**1**	**2**	**3**
ZhEoZP	24.6	18.5	14.6	12.0
(ZhEo)ZP	37.0	19.6	12.7	9.1

From this data, it can be seen that the lowest level of solids entering the ozone stage is achieved using the ZhEoZP sequence. It is noteworthy, however, that the difference in solids buildup is very small when eliminating the Zh washer.

Data by Patt, et.al., and others suggest that incremental ozone use per kg of COD is in the range of 0.1-0.2 kg ozone/kg COD.(7,10) For reference, the COD equivalent of 12.7 kg total dissolved solids/t is about 10 kg COD/t. This is about the equivalent of an additional 1.25 kg ozone/t, or, at 1200 madtpd, an additional 62.5 kg ozone/hr. A lesser increment of ozone use will be required for the second, medium consistency, ozone stage.

Impact on Thermal Balance

The trend in bleach plant design over the last 20 years has been toward operating at increasing temperatures throughout the bleaching operation. Conventional chlorination stages were typically cooler as it was not necessary to increase its temperature beyond that which occurred due to normal filtrate recycle. Over the years the typical temperature in the bleach plant has continued to rise due to hotter incoming pulp temperatures, and the use of increasing amounts of filtrate recycle in the bleach plant.

As filtrate is recirculated back to recovery from the bleach plant, the solids level in the filtrates rises at each washing step, the lowest being at the final bleaching stage, and continuously increasing to the highest level at the first brown stock washing stage. The projected levels of solids entering the ozone stage at various levels of filtrate recycle has been described in the last section. The thermal balance would follow an identical trend, if there were no heating or cooling of the pulp in the bleaching stages. In the case of an OZEoZP bleach plant with all but 2m^3/t recycled to recovery, the temperature in the ozone stage would rise to over 70°C, assuming the Eo stage were to be operated at a temperature of 70°C.

Published data on the quantitative impact of temperature on the performance of an ozone stage is inconsistent (2,10). This is likely due to the variations in solids (COD) carryover to the ozone stage in various laboratory and pilot plant reported results. However, all references indicate that there is a negative impact on delignification and selectivity with increasing temperature. This then requires that the ozone stage must be cooled to achieve optimum ozone stage performance. Although performance improves as the temperature is reduced, the practical limit of operating temperature in commercial operation is 40-50°C.

The energy required for cooling pulp due to the incorporation of the ozone stages in the OZEoZP sequence, as well as the steam required for operation of the other bleaching stages is shown in Tables 9 (cooling energy) and 10 (steam use). The operating temperature of the ozone stage is 40°C, and all other stages are as noted in parentheses in the steam use table. Full countercurrent washing is practiced with a dilution factor of 2.0, and the acid purge rate is 2m^3/t. In addition to the energy required for cooling the pulp, the generation of ozone gas requires that the dielectrics of the ozone generator be cooled to maximize the efficiency of production of ozone. The energy required for cooling the ozone generators at a consumption of 6.5 kg ozone/t is shown separately, but included in the total energy use for the bleaching sequence.

Table 9: Cooling Energy Required

	OZEoZP	O(ZEo)ZP	ODEoD
Cooling Required(MJ/madt)			
Pulp			
Z_1 Stage	412.9	407.5	—
Z_2 Stage	408.5	406.9	—
Ozone Generation	201.5	201.5	—
TOTAL (MJ/madt)	1022.9	1015.9	0

The cooling required for operating the OZEoZP or ODEoD sequence is shown on Table 9. There is no cooling required for the conventional ODEoD sequence, so all of this incremental energy is due to the incorporation of the ozone stages. The relatively cool ozone stages are placed between two hot stages, so the cooling demand for using two ozone stages is about twice that than for using one ozone stage, for example, in an OZEoP sequence. The cooling required for ozone generation is directly proportional to the ozone charge. There is no significant difference between the OZEoZP and O(ZEo)ZP sequences.

Depending on the local conditions at the mill, the capital and operating cost to incorporate the cooling system for both the pulp and ozone generation side may be moderate or substantial. This is highly variable and based on local climactic conditions and the cost of incremental power.

Table 10 Steam Use

	OZEoZP	O(SEo)ZP	ODEoD
Steam Use (kg/madt)			
Oxygen Stage (95°C)	170.3	153.3	117.4
D_1 Stage (60°C)	—	—	49.2
E_o Stage (70°C)	119.9	134.3	50.5
D_2 Stage (70°C)	—	—	160.6
P Stage (70°C)	95.5	95.5	----
TOTAL (kg/madt)	385.7	383.1	377.7

The steam use for either the OZEoZP or ODEoD sequences is quite similar. In the D1 stage of the ODEoD sequence, the pulp is not heated by steam, but the energy required to preheat the chlorine dioxide solution is included to obtain a proper comparison of total energy use. However, this would normally be accomplished by use of a heat exchanger operated using the Eo stage effluent. In this case, the total steam required for ODEoD sequence would be 305.0 kg steam/t, or about 25-30% less than either the OZEoZP or O(ZEo)ZP sequence.

Impact on Recovery

The implementation of oxygen delignification has been accomplished at many mills throughout the world, and the dissolved solids released in the oxygen stage and inorganic solids added to the stage are recycled to recovery. In practicing non-chlorine bleaching in a ZEoZP sequence downstream of an oxygen stage, the amount of organic solids recycled to recovery is similar to that of an oxygen stage. The inorganic fraction, however, is significantly lower, as the main oxidants (ozone and peroxide) are converted to CO, CO_2, and H_2O, so does not add to inorganic load.

Quantitatively, this impact is summarized in Table 11.

Table 11: Impact on Recovery

Dissolved Solids (kg/madt)

	Organic	Inorganic	Total
Generated/Applied			
Oxygen (O)	20.0	28.2	48.2
Ozone (Z)	9.7	5.0	14.7
Extraction (E)	9.6	4.0	13.6
Peroxide (P)	4.3	10.0	14.3
	43.6	47.2	90.8
Losses			
To sewer	10.5	10.4	20.9
With pulp	0.9	2.6	3.5
To recovery	32.2	34.2	66.4
Pressate purge: $2m^3$/madt			
Water on P washer: DF = 3.0			
Water make-up on O_2 washer: $2m^3$/madt			

The balance between sodium and sulfur in a kraft cooking liquor system is maintained at an equilibrium level which is determined by the loss and the makeup. The implementation of ozone bleaching, and recovery of bleach effluent into the cooking liquor system significantly impact the sodium/sulfur balance. Since the ozone bleaching stage is carried out at a pH of 2-3, an acid such as sulfuric acid is added to the pulp prior to the ozone reactor. Some of the acidic effluent generated in the ozone stage will have to be purged from the system so that dissolved metal ions can be removed from the system. However, the majority of the acidic effluent will be used as the wash water for the preceding stage. In other words, the majority of the sulfur applied on the pulp in the form of sulfuric acid will be eventually recovered into the liquor system. Further, the implementation of a total chlorine-free bleaching sequence such as OZEoZP would allow the complete counter-current washing of entire fiber line with the exception of purging of the acidic effluent. The sodium hydroxide applied in the E and P stages will also be introduced to the cooking liquor system.

Consequently, makeup chemical situation will be directly determined by the amount of sodium hydroxide and sulfuric acid applied in the bleach plant in a closed total chlorine-free bleached pulp mill.

A quantitative evaluation of mill sodium/sulfur balance and white liquor inventory was assessed and published in the Proceedings of the 1993 Non-Chlorine Bleaching Conference.(11) By using this model, the future makeup chemical situation at various chemical application levels in the bleach plant can be estimated.

Most of the chemicals carried over to the bleach plant will be recovered into the pulping liquor system since the bleach washers will be integrated into the counter current washing scheme of the entire fiber line. The chemicals carried out by the bleached pulp in the form of liquid are the chemicals contained in the pulp off the P-Stage washer. The other significant source of loss is the acidic effluent purged from the ozone stage which is one of the operating variables evaluated. Sources for sodium and sulfur input to the system aside from the makeup chemical to the recovery system and sulfur input to the lime kiln introduced by the fuel were sulfuric acid applied at the ozone stage and sodium hydroxide applied at the extraction and peroxide stages in the OZEoZP sequence. The sodium hydroxide required at the oxygen stage was supplied as oxidized white liquor, thereby eliminating the implication on mill sodium/sulfur balance. Makeup or removal of sodium and sulfur required at the recovery system is determined by the overall balance of these elements.

The inventory adjustment requirement in the recovery cycle is shown in Table 12 when 10 kg H_2SO_4 is used in the bleach plant. This table describes the impact of both alkali use as well as effluent purge in the overall balance. Note that the sodium/sulfur balance is very sensitive to small changes in bleach chemical use as well as the purge rate.

Table 12 Inventory Adjustment Requirement
(at 1.0% H_2SO_4 to ozone stage)

		Acid Effluent Purge (m3/t)			
Make - Up		**0.00**	**2.00**	**4.00**	**6.00**
NaOH = 1.0%	$NaSO_4$	-4.68	0.25	2.90	5.62
H_2SO_4 = 1.0%	S	0.00	0.00	0.00	0.00
	NaOH	1.10	2.21	3.14	3.96
NaOH = 1.5%	$NaSO_4$	-11.60	-1.98	2.93	4.40
H_2SO_4 = 1.0%	S	2.23	0.72	0.00	0.00
	NaOH	0.00	0.00	0.61	2.10
NaOH = 2.0%	$NaSO_4$	-20.47	-8.15	-0.44	4.40
H_2SO_4 = 1.0%	S	5.11	2.72	1.09	0.00
	NaOH	0.00	0.00	0.00	0.24
NaOH = 2.5%	$NaSO_4$	-29.35	-14.30	-4.90	1.50
H_2SO_4 = 1.0%	S	7.99	4.71	2.53	0.94
	NaOH	0.00	0.00	0.00	0.00

For the case of the OZEoZP sequence described, the acid use is just over 1.0% (10 kg/t), and the alkali use is between 1.5-2.0% (15-20 kg/t). According to this balance, at the minimum purge rate of 2 m3/t, it will be necessary to remove about 6.7 kg Na_2SO_4/t while adding about 2.3 kg S/t in order to maintain the sodium/sulfur balance in the recovery cycle. A much closer balance is achieved at a purge rate of about 4.2 m3/t purge rate, where sulfur will have to be added at a rate of about 1 kg S/t.

However, it is the objective of the plant design to minimize the outfall from the bleach plant, so increased purge rate is undesirable. In addition, the sodium/sulfur balance will be difficult to maintain since the sulfidity of the liquor will change quite significantly with small changes in acid and alkali use in the bleach plant. With tight system integration, it is likely that real time simulation programs will be necessary to control sulfidity in the effluent free mill.

It is desirable, therefore, to consider replacement of some or all of the NaOH requirement with oxidized white liquor. The use of oxidized white liquor for oxygen delignification is now done as a common practice, and possibility of using it as the source of sodium hydroxide used at the extraction stage has also been proposed.(12) There is no report on detrimental effects on pulp quality associated with the use of oxidized white liquor in the conventional bleaching sequence.

Table-13 shows the theoretical composition of oxidized white liquor when a white liquor with 6.5lbs.Na_2O/ft^3 active alkali is oxidized at 90% efficiency. According to this example, the use of 1.0kg of NaOH in the form of oxidized white liquor is equivalent to 0.92kg of Na and 0.15kg of sulfur inputs to the system. In the case of 2.0% NaOH (11.5kg.Na/t) and 1.0% H_2SO_4 (0.32kg.S/t) application to the OZEoZP system, the excess amount of Na in the liquor system will be 3.07kg/t if $2.0m^3/t$ of acidic effluent is purged. Therefore, the replacement of about 25% of the total NaOH required for the E-stage with the NaOH in the form of oxidized white liquor will be sufficient to maintain the Na balance in the liquor system. Balance of sulfur requires further analysis since some of the sulfur introduced at the E-stage may be lost with the final bleached pulp, which is not taken into consideration in this simulation program.

Table 13 Oxidized White Liquor Composition

	as Chemical (lbs/cft)	as Na (lbs/cft)	as S (lbs/cft)
Na_2S	0.25	0.15	0.10
NaOH	7.00	4.03	0.00
Na_2CO_3	3.33	1.45	0.00
Na_2SO_4	0.49	0.16	0.11
$Na_2S_2O_3$	2.23	0.65	0.90

(White liquor AA = 6.5, Sulfidity = 30%, Reduction 90%)

The use of oxidized white liquor as the source of NaOH used in a total chlorine free sequence such as OZEoZP may present some potential problems which did not occur with conventional sequences. One obvious possibility is the creation of TRS emission when the alkaline effluent reaches the acidic stage in the counter current washing scheme. Another possibility is the loss of brightening power of hydrogen peroxide since sodium thiosulfate exists in the oxidized white liquor reacts with hydrogen peroxide.

These problems may be solved by adopting a white liquor oxidation system that allows complete oxidation of sulfur compound and some commercial systems are now in operation for 100% reduction of $Na_2S_2O_3$ to Na_2SO_4.

One other possibility which may be more critical is the introduction of metal hydroxides into the filtrate system which reach the acidic pre-ozone thickener or the alkaline peroxide stage where metal ions will be detrimental. Since metal hydroxides in white liquor exist as suspended solids, filtration of oxidized white liquor may be required in order to successfully utilize it an ozone/peroxide bleach plant. The results of removal of metal ions from white liquor by filtration are shown in Table 14.(13)

Table 14: Efficiency of Removal of Metal Ions in Filtration of White Liquor

Metal Ion	Removal Efficiency
Calcium	96%
Iron	91%
Zinc	63%
Manganese	16%
Nickel	8%
Magnesium	7%
Cobalt	3.5%
Copper	2.6%
Aluminum	0.9%
Chromium	0.4%

The filtered residue from the filtration of white liquor comprised 0.84% organic matter, 5.07% carbonates (burnt CO_2), 55.64% silica, 30.9% analyzed metal ions, and 7.55% other ions (sulfur, etc.). Filtration of white liquor may be a partial answer, but considering the slimy nature of metal hydroxide and the harsh conditions of the white liquor, this may be a challenging technology to be investigated.

Another possible approach for solving the mill sodium and sulfur balance would be the generation of NaOH and H_2SO_4 from the Na_2SO_4 removed from the liquor system. Systems of this type are in various stages of development from lab/pilot scale (Bipolar Membrane Electrodialysis developed by Paleolougu et al.(14) as well as early commercial systems associated with reprocessing of Na_2SO_4 from chlorine dioxide generators. The on-site splitting of saltcake into sodium hydroxide and sulfuric acid is attractive since they are the expected makeup chemicals in a future total chlorine free bleached pulp mill. For example, in the case of 2.0% of NaOH and 1.0% of H_2SO_4 are applied to the OZEoZP system, about 8kg/t of saltcake will have to be removed from the liquor system according to Table-10. The splitting of this purged saltcake would result in 4.4kg/t of NaOH and 5.6g/t of H_2SO_4 assuming perfect stoichiometry. In other words, about 20% of NaOH and 56% of H_2SO_4 required in the bleach plant can be obtained from the purged saltcake.

Bleaching Chemical Use/Cost Summary

This evaluation has provided the background to evaluate the bleaching chemical cost of two new sequences - one ECF and one TCF - both using ozone and peroxide as major oxidants, and compare them to a conventional ECF sequence. The following tables summarize the bleaching chemical costs. Although not in the scope of this paper, there is a further impact on steam and power comparing these sequences, particularly since it is necessary to operate the ozone stages at a relatively low temperature.

Table 15: Bleach Chemical Use/Cost for OZEoZP Sequence

	Chemical Applied (kg/madt)	Chemical Cost ($US/kg)	Bleach Chemical Cost (US$/madt)
Oxygen (O_2)	21.0	0.05.	1.05
Sodium Hydroxide (NaOH)	19.0	0.30	5.70
Ozone (O_3)	6.5	1.20	7.80
Sulfuric Acid (H_2SO_4)	19.4	0.05	0.97
Hydrogen Peroxide (H_2O_2)	15.0	1.05	15.75
TOTAL	-	-	$31.27

Table 16: Bleach Chemical Use/Cost for OZPD Sequence

	Chemical Applied (kg/madt)	Chemical Cost ($US/kg)	Bleach Chemical Cost (US$/madt)
Oxygen (O_2)	16.0	0.05	0.80
Sodium Hydroxide (NaOH)	7.5	0.30	2.25
Ozone (O_3)	5.2	1.20	6.24
Sulfuric Acid (H_2SO_4)	19.4	0.05	0.97
Hydrogen Peroxide (H_2O_2)	12.0	1.05	12.60
Chlorine Dioxide (ClO_2)	5.0	1.00	5.00
TOTAL	-	-	$27.86

Table 17: Bleach Chemical Use/Cost for ODEoD Sequence

	Chemical Applied (kg/madt)	Chemical Cost ($US/kg)	Bleach Chemical Cost (US$/madt)
Oxygen (O_2)	19.0	0.05	0.95
Sodium Hydroxide (NaOH)	17.0	0.30	5.10
Chlorine Dioxide (ClO_2)	15.4	1.00	15.40
TOTAL	-	-	$21.45

Notes on Tables 15, 16, and 17

1. Cost of bleach chemicals does not include the cost of capital.
2. Cost of oxidized white liquor not included as the cost is the same for all sequences evaluated.

The lowest cost for bleaching this pulp is the use of the reference ODEoD sequence, based upon the typical chemical costs shown. In order to offer TCF pulp pulp for the market, it is necessary to accept an increase in bleaching chemical cost. With the use of a small amout of chlorine dioxide and operating the OZPD sequence, a savings of about $US 3.50/madt can be realized.

Conclusions:

1. The OZEoZP sequence is capable of producing a 90+% ISO brightness (88+% ISO brightness) pulp from Brazilian eucalyptus which has been cooked to a kappa number of less than 12 in an extended delignification process.
2. The strength of the TCF produced pulp is comparable to a conventional ECF pulp produced in an ODEoD sequence, being equal or within 10%, even though the viscosity of the TCF pulp is substantially lower.
3. The OZPD sequence is an attractive sequence for production of ECF pulps for those mills with available chlorine dioxide capacity and without the stringent requirement to use no chlorine compounds in the bleaching.
4. Integration of ozone bleaching system in a total chlorine free bleach plant will allow almost complete counter current washing of the entire fiber line. However, it may necessitate the removal of excess saltcake from the liquor system depending on the chemical application level in and the acid purge volume from the bleach plant.
5. Control of white liquor sulfidity and inventory may require the use of dynamic simulators to predict effects due to changing use of NaOH and H_2SO_4 in an OZEoZP bleach sequence.
6. Splitting of purged saltcake into sodium hydroxide and sulfuric acid may be pursued in order to maintain the overall sodium and sulfur balance in the liquor system.
7. The use of oxidized white liquor for the extraction and peroxide stages to maintain the sodium/sulfur balance is attractive, and filtration of the white liquor to allow this is a natural choice for this improvement.

Experimental

Pulp Sample:

The pulp sample was prepared from eucalyptus chips from the Riocell S.A pulp mill in Guaiba, RS, Brasil, in the laboratory by batch cooking with extended delignification. The unbleached pulp had a kappa number of 11.6 with a viscosity of 44.1 (TAPPI T-230).

Oxygen Stage (O):

Bomb reactor, 12% od consistency, 60 minutes, 90°C, 0.1% Mg on od pulp, 1.6% NaOH on od pulp, 100 psig.

Ozone Stage (Z):

Screw reactor, pulp acidified to pH=2.0 and pressed to 40% od consistency, fluffed, and contacted for required retention time to consume desired charge of ozone on od pulp, end pH=2.5.

Oxidative Extraction Stage (Eo):

Bomb reactor, 12% od consistency, 60 minutes total (with first 10 minutes at 60 psig), 71°C, end pH=12.2.

Peroxide Stage (P):

Polyethylene bags immersed in water bath to maintain constant temperature, 12% od consistency, 70°C, 180 minutes.

FAS (formadine acid sulfimic):

Polyethylene bags immersed in water bath to maintain constant temperature, 12% od consistency, 70°C, 90 minutes.

Chlorine Dioxide Stage (D):

Polyethylene bags immersed in water bath to maintain constant temperature, 12% od consistency, 70°C, 180 minutes.

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