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A Mill Experience using Acid and Ozone Stage for Eucalyptus Pulp Bleaching – A System Closure Vision

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Resumo

O objetivo deste estudo e reportar a experiência operacional da Votorantim Celulose e Papel (VCP) depois da implementação em sua linha de branqueamento de um estágio ácido à quente, antes do estágio de ozonólise.

A avaliação da implementação do estágio ácido ocorreu em três diferentes sistemas de filtrado, (1) sem estágio ácido e ciclo de filtrados fechado (período referência), (2) com estágio ácido e circuito de filtrados fechado e (3) com estágio ácido e circuito de filtrados aberto.

O estágio ácido resultou em uma redução em torno de 3 unidades do número kappa da polpa. O estágio de ozônio sofreu uma redução de 43% em sua eficiência de deslignificação quando o estágio ácido foi implementado.

A implementação do estágio ácido resultou em uma eficiente remoção dos metais da polpa, mas nenhum impacto na planta de recuperação foi diagnosticado, mesmo utilizando um sistema de filtrados fechado, o qual gerou um maior teor de íons cloreto no sistema. A intensidade de incrustações à base de oxalato de cálcio foi reduzida significativamente, com a implementação do estágio ácido. Mas, ainda existe uma dúvida : O que fazer com o filtrado do estágio ácido?

Palavra Chaves : Branqueamento, Estágio Ácido, Fechamento de Circuito

Abstract

Votorantim Celulose e Papel (VCP) is a brazilian company that produces Market Bleached Kraft Pulp. VCP has recently implanted a acid stage in the bleaching plant of Jacareí Mill, for the removal of hexenuronic acids.

The evaluation of implementation of the acid stage occurred in three different filtrate cycle systems, (1) without acid stage and close filtrate cycle (reference period), (2) with acid stage and closed filtrate cycle and (3) with acid stage and open filtrate cycle.

The acid stage provide an significant reduction of kappa number of pulp, around of 3 units. The ozone stage suffered a decrease of the 43% in your delignification efficiency when the acid stage was implanted.

The implementation of acid stage result in a efficient removal of metals from the pulp, but anyone impact in the chemical recovery plant was contemplated, same using a filtrate cycle system that to provided the inlet of higher chloride ions contents in recovery plant. The incidence of oxalate scaling was reduced significantly with acid stage implantation.

Key-words: acid stage, bleaching, hexenuronic acids, closed cycle

Introduction

To one decade behind, had as principal objective of studies of pulp and paper research groups, the causes of the variation of the bleachability among different pulps. Quality wood, pulping technologies, unspecified bleaching chemicals and washing systems were the principal evaluated causes. Until that moment, there were a lot of controversy and doubts, on the one that real and significantly, it influenced the bleachability of unbleached pulp. In 1977, it was discovered the existence of reactions that provide hexenuronic acids during alkaline pulping. These acids possess the property of form covalent bonds with lignin, consume electrophilic bleaching reagents, bind to metal ions and cause brightness reversion of bleached pulps. Of this discovered, some appeared explanations for the bleachability problems of different pulps, besides elucidations for the brightness reversion and oxalate scaling problems.

The use of the acid stage for removal hexenuronic acids from the pulp was suggested in 1995, and your results showed a total removal of these acids, without great variations in the quality of the bleached pulp. However, doubts exist yet. For example, which the performance of the acid stage use for eucalyptus pulps? Is there real gains in the bleachability of the pulp? What to do with the filtrate of this stage? Open it to effluents treatment plant, or recycle it in the bleaching plant? Is the quality of the bleached pulp really unaffected with the acid stage utilization? The results obtain in laboratory repeat in industrial scale?

Votorantim Celulose e Papel (VCP) is a brazilian company that produces Market Bleached Eucalyptus Kraft Pulp. VCP, in the Jacareí Mill, started-up a new fiber line in June 1997, with the OQOpZ(DnD) bleaching sequence. In August 1998, this sequence was converted to OOZ(DQ)(PO), due at high chemical consumption, low production rates and quality instability. Recently, the VCP retrofit this same sequence, adding a acid stage converting it into the (OO)AZD(PO) (Rodrigues et al, 2000).

The objective of this paper is to show the impact of the acid stage (1) in the bleaching filtrates lay-outs and (2) in the ozone bleaching performance.

Implementation of the acid stage in the VCP-Jacareí Mill

In August of 1998, one of the industrial plants of VCP-Jacareí had your bleaching sequence converted of OQOpZ(DnD) to OOZ(DQ)(PO). This modification was accomplished due to the high consumption of bleaching chemicals and to the production instability and quality of the final product. The main objectives of this modification were reached, but other problems still existed to be solved. Such problems included: (1) the number kappa of pulp from digester had to be maintained in a lower level, to reach an acceptable variable cost; (2) the ozone stage possessed a low delignification efficiency and serious problems with oxalate scaling and (3) the bleaching plant was one of the bottlenecks for any increase of mill production.

The evaluation of the acid stage in the sequence OOZ(DQ)(PO), it was accomplished by simulations using industrial pulps. From the results obtained at laboratory, in September 2000, there was the acid stage implementation in the bleaching line B of VCP-Jacareí, originating the (OO)AZD(PO) sequence. The illustrations of the bleaching line, before and after the acid stage implementation, are in figures 1 and 2, respectively.

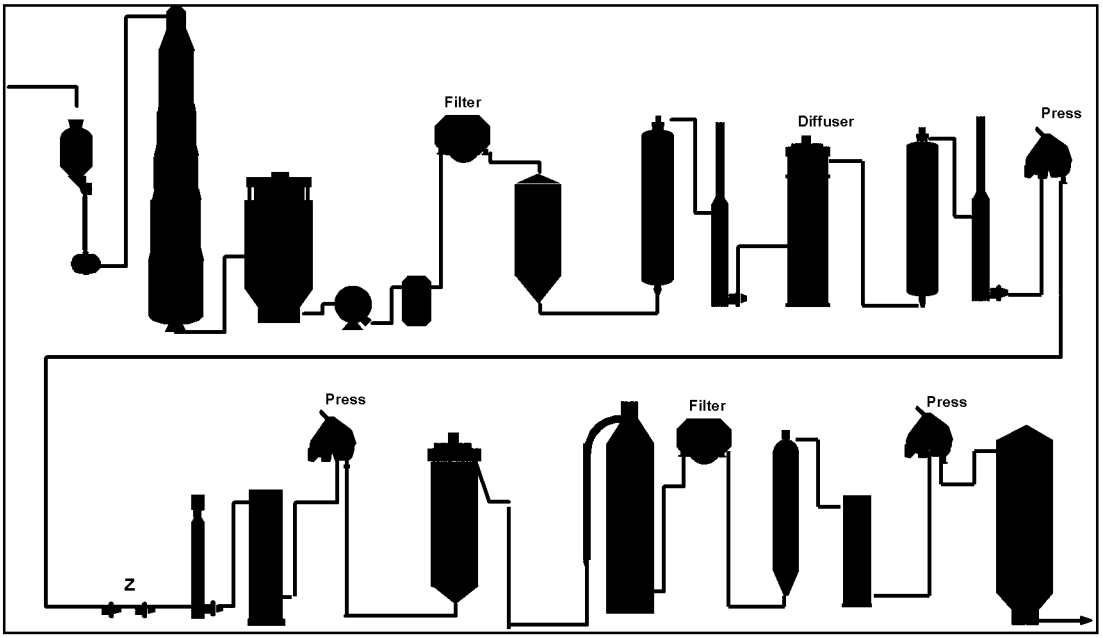

Figure 1 – The layout of bleach plant before the acid stage implementation

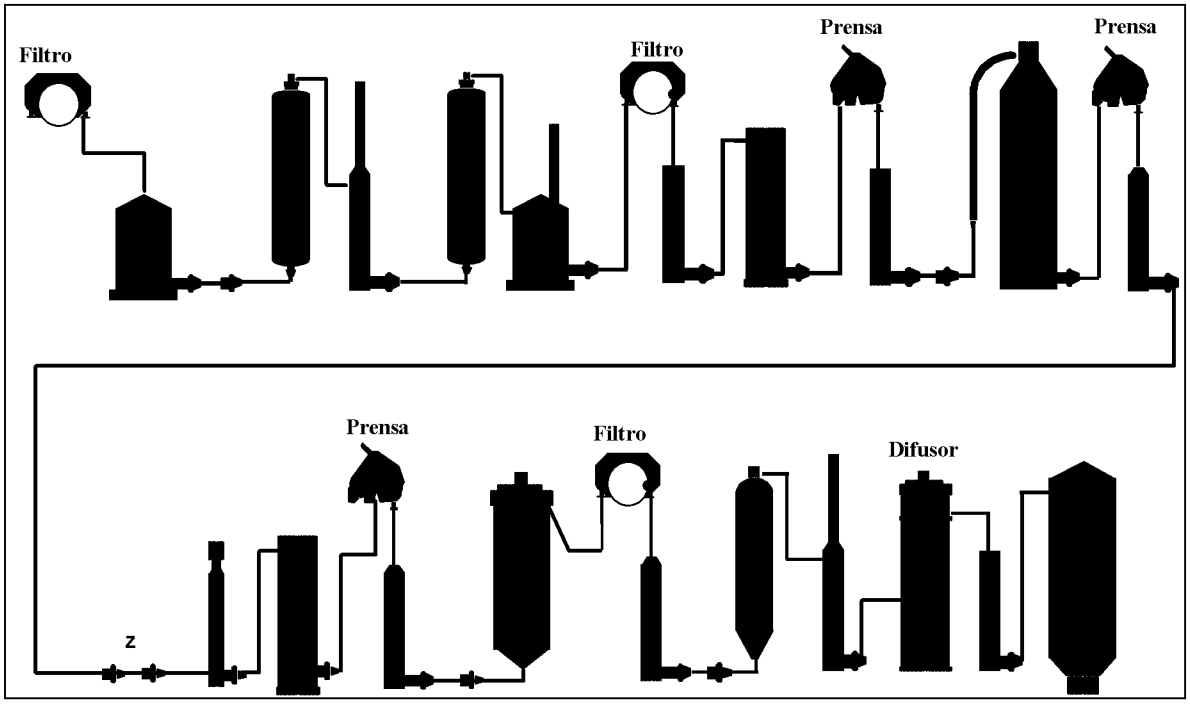

Figure 2 – The layout of bleach plant after the acid stage implementation

One of the doubts during the implementation of the acid stage, was the filtrate bleaching system, it would stay closed or not. The evaluation of the results was accomplished in 3 periods described as:

Table I – Description of periods evaluated

Periods	Description
(1)	reference – without acid stage
(2)	with acid stage and closed cycle
(3)	with acid stage and open cycle

In figure 3 is showed the filtrate bleaching system for the three evaluated periods.

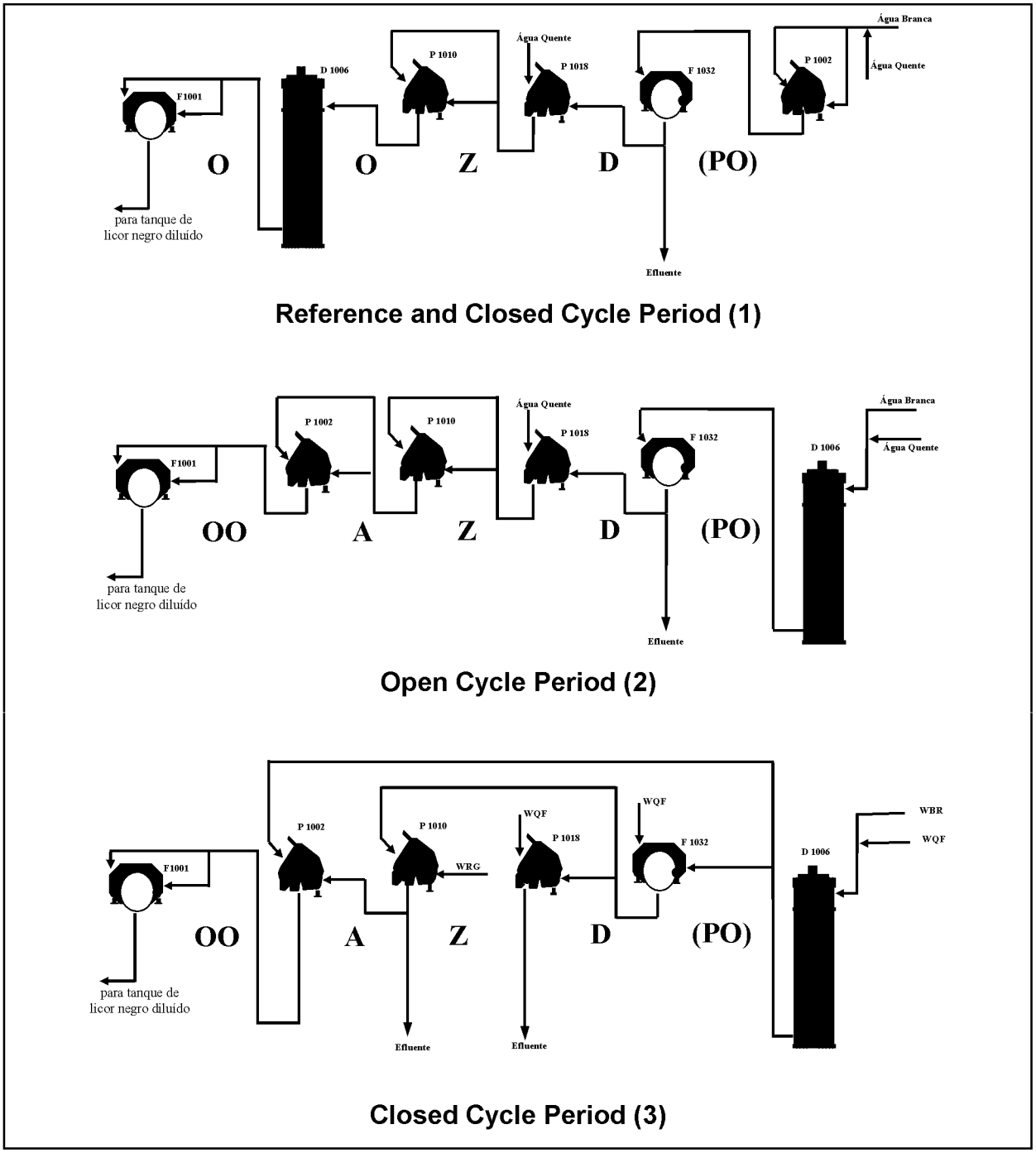

Figure 3 – Filtrate bleaching systems evaluated

The performance of the acid stage

In the Table II, is shown the data of acid stage efficiency in the different periods evaluated.

It is observed that the alteration in the filtrate cycles, practically didn't affect the drop of number kappa in the acid stage. However, there was a significant increase in the drop of the viscosity, when the filtrate cycle was open, increasing from 87 to 129 points.

Table II – Acid stage performance

Periods	Pré–O_2		Acid Stage			
	kappa number	viscosity dm³/kg	kappa number	viscosity dm³/kg	Δ kappa	Δ visc.
(1)	9,5	1034	-	-	-	-
(2)	10,3	1076	7,5	989	2,8	87
(3)	10,4	1144	7,7	1015	2,7	129

The higher drop in the viscosity in the open filtrate cycle mode, probably is due at the higher use of sulfuric acid in these circumstances. In spite of the pH of the reaction the same, the application of a larger volume of sulfuric acid it could damage the fiber in the moment of your application. The substitution in the use of an acid filtrate for an alkaline one in the showers of the washing press, before the acid stage, is the responsible for the largest requiremente of sulfuric acid.

The higher susceptibility of drop in the viscosity in the acid stage, provide the use of mild conditions, as lower temperature and higher pH.

The efficiency of the ozone stage

In the Table III, the results can be visualized obtained in the ozone stage, in the evaluated periods.

The delignification efficiency was calculated by the ratio between the drop of kappa number and the ozone charge applied in the ozone stage. The ozone charge was of 4,7 kg/adt to the period (1), 3,8 kg/adt for the period (2) and 4,7 kg/adt for the period (3).

Table III – Ozone stage performance

Periods	Kappa Number			Z Stage Efficiency
	Acid Stage	Z Stage	Δ Kappa	D.E.*
(1)	-	6,0	3,5	0,74
(2)	7,5	5,9	1,6	0,42
(3)	7,7	5,7	2,0	0,43

*delignification efficiency

There was a significant drop in the delignification efficiency, about 43%, when the acid stage was implemented in closed filtrate cycle. The low efficiency in the ozone bleaching sequence produced a delta kappa of only 1,6, compared with a delta kappa of 3,5, in the process reference.

Practically, the ozone didn't react with the pulp, what took to reduce the applied charge of 4,7 for 3,8 kg/adt. The reduction in the ozone charge was necessary due at requirement in to reduce the risk of disable of the ozone production plant, provide by high ozone residual in the vent ozone destruction unit.

The opening of filtrate cycle didn't promote any increase in the performance of the ozone stage, where the delignification efficiency was around 0,43. It is important to say that together with the opening of the circuit of filtrates, there was also, the substitution of filtrate for flesh water, in the screw of the press before the ozone stage. This substitution impair any more coherent comparison among the evaluated periods, since there is a positive impact, due to a reduction in the COD load in the pulp entering in the ozone mixers.

The higher drop in the ozone stage efficiency provided by the acid stage use, it is of difficult rationalization. But, we could suppose the following hypothesis: " The gas ozone reacts more quickly with the hexenuronic acids than with the lignin, for reasons of facility accessibility". This hypothesis is based, in the fact of the hexenuronic acids are linked to the xylans, and these are in the most external areas of the cellular wall of the fiber, what promotes a higher accessibility of bleaching chemicals, in our case, the ozone. The lignin in this stage of the process, stay in sites inside of the cellular wall, what impair your accessibility ".

Calcium oxalate scaling

Scaling is a serious problem for the pulp mills, bringing damages, as (1) production loss, (2) loss of the operational control, (3) increase in the consumption of bleaching chemicals, (4) expenses with chemical and mechanical systems cleanings, and (5) dirt in the bleached pulp. Of the several scaling types that can happen, four are considered main, to know: (1) carbonate of calcium, (2) oxalato of calcium, (3) barium sulfato and (4) pitch.

Calcium oxalate scaling are the hardest and difficult of removing once deposited on a surface (Ester, 1994). The calcium oxalate is originating from the wood, and of reactions of the ion calcium with the oxalic acid. The oxalic acid comes from the reactions of bleaching chemicals with the pulp, being your more intense formation in the ozone stage. In mills producing pulp from hardwood, the formation of oxalic acid tends to be higher, due, mainly, to the largest amount of hexenuronic acids in your constitution. Calcium ions is coming of the wood and of the white liquor clarification.

Starting from December 1998, VCP-Jacareí began to live problems with oxalate scaling in the bleaching plant, more specifically, in the ozone stage wash press. The situation was critical, to the point of shutdown for hydroblasts cleaning with pressure of up to 950 kg/cm^2, no more solving.

The figure 4 compares the values of calcium oxalate, presents in the pulp suspension feeding of the ozone stage wash press, during the periods (1) and (2).

It is observed that the acid stage implementation reduced from 2,01 to 0,92 kg/adt, the amount of calcium oxalato in the pulp suspension feeding the ozone stage wash press. The low level of calcium oxalate reached in this point, after the acid implementation, it allowed to reduce the frequency of the hydroblasts cleanings and, consequently, the associated costs.

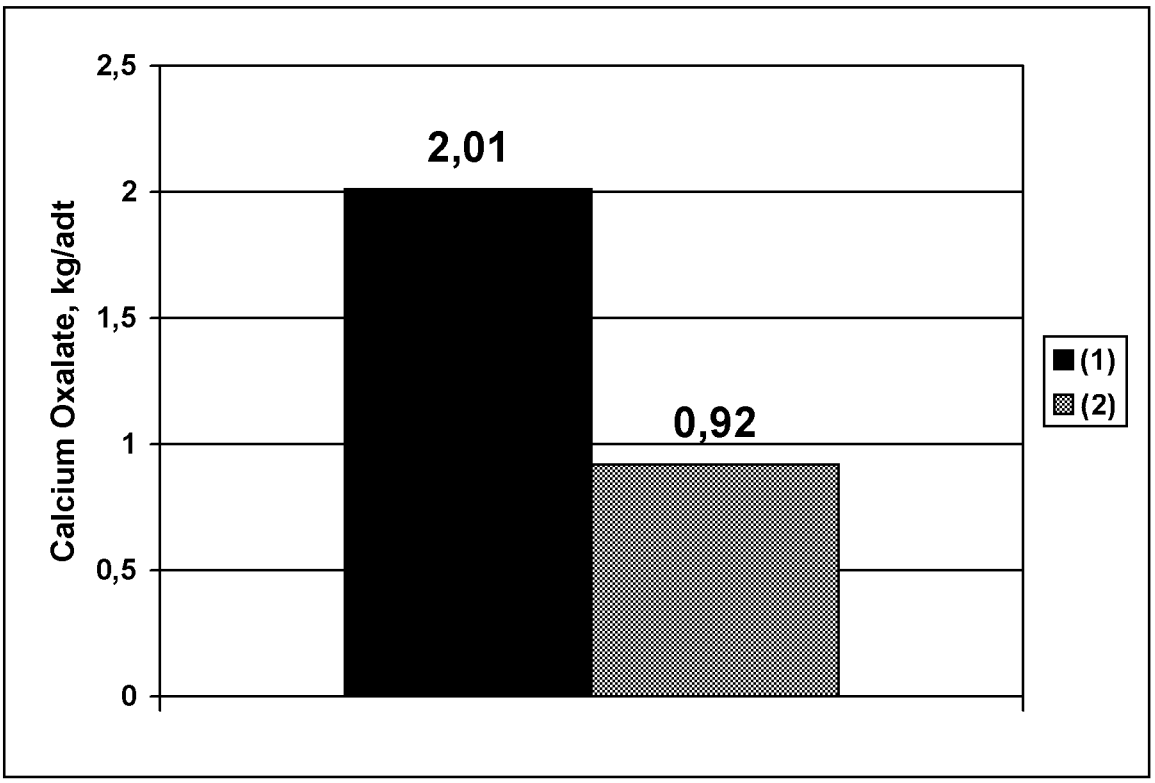

Figure 4 – Acid stage effect on calcium oxalate contents in the pulp suspension feeding ozone stage wash press

Non-process elements levels (NPE)

The chemical elements that enter in the process of pulp production, with the wood, water and chemical inputs, staying accumulate in the calcium and sodium cycles, are called non-process elements. These elements include potassium, phosphor, magnesium, manganese, iron, aluminum, silica, calcium, barium and chlorine.

In the table IV, the results of some non-process elements are presented. These results are from the previous oxygen washer filtrate, used in the washing zone of digester, and later, pumped to the chemical recovery plant.

For a appropriate understanding, the filtrate of the period (1) comprises all the elements dissolved in the oxygen delignification stage and of the ozone stage. In the period (2), the filtrate contains elements dissolved in the oxygen delignification stage, acid and ozone stages. In the period (3), the filtrate that comes back to the digester, it possesses the elements only dissolved in the oxygen delignification stage and peroxide stage (please, to see figure 3).

Table IV – Non-process elements content in Pré-O_2 filtrate

	Non-process elements, ppm						
Periods	**Ca**	**Mg**	**Fe**	**Mn**	**K**	**Cl**	**SS[1], %**
(1)	21,5	17,0	4,3	2,6	581	25,0	2,79
(2)	38,4	37,8	13,1	4,9	318	22,1	2,68
(3)	16,9	31,9	5,3	2,9	170	181	1,47

[1]SS- soluble solids

It is observed that when the acid stage was implemented, still with the filtrates bleaching cycle closed (2), except the elements potassium and chloride, all the other elements had your high contents. The explanation is that the acid stage promotes a metals leaching of the pulp, according Vuorinen, et al, 1996.

The magnesium suffered a significant increase after the acid stage implementation. The reason for this increase is that besides the leaching in the acid stage, in the period there was also an increase in the talc charge (magnesium silicate/oxide) in the process, due at largest pitch incidence in the washing presses.

It is observed that when the filtrate bleaching cycle is opened (3), the level of the non-process elements in the filtrate was reduced. This behavior was already expected, since every element leached in the acid stage it was discharged for the effluent. However, the magnesium amount, suffered only a small reduction, what is explained by the return of the magnesium sulfate from peroxide stage filtrate. This filtrate, previously discharged to the effluent, it has been used in the showers of post oxygen press, that comes in counter-current until the digester wash liquor tank storage. As consequence, the content of chloride ions, after the opening of the circuit of filtrates, increased significantly, changing from 25 to 181 ppm. The reason for this increase, is the contamination of chlorides present in the filtrate of the peroxide stage.

Chloride and potassium are impartial elements when into the chemical recovery plant, dragged by the black liquor (Ulmgren, P., 1996). They reduce the sticky temperature of the deposit formed in the tube banks in the recovery boiler. The reduction of this temperature does with that increases the intensity of formation of deposits in the boiler tubes, what results in increase of the number of shutdown for cleaning of the same ones.

For a better evaluation of the impact of the chloride in the chemical recovery plant of the pulp mill, it was made a monitoring of the chloride contents in several points of the system (Table V).

It is observed that the return of the peroxide stage filtrate, didn't have significant impact in the chemical recovery plant. The levels of chloride were practically the same ones, in the diluted and concentrated black liquor, in the dust from recovery boiler, economizer and of the CRP, and in the concentrated white liquor. If the values stay in these levels, the alternative of the use of the filtrate of the peroxide stage, seen by this parameter, it can be definitive.

Table V – Chloride contents in chemical recovery plant

Chemical Recovery Plant Locations	**Chloride Contents in the Periods (%)**		
	(1)	**(2)**	**(3)**
Weak Black Liquor	1,8	1,6	1,5
Strong Black Liquor	5,6	2,0	1,5
Recovery Boiler Dust	3,2	4,2	4,2
Economizer Dust	3,1	4,2	4,3
CRP Dust	6,7	5,3	5,9
Strong White Liquor	3,0	2,5	2,0

The modifications in the bleaching plant, had influenced the sodium/sulfur balance of the chemical recovery system. A unbalancing occurred due to the discharge to the effluents of great part

of the sodium and sulfur ions, that previously returned for the circuit of liquors. The sodium is still, usually restored by the alkali added in the oxygen delignification stage. The replacement of the sulfur became more problematic, causing drop in the sulfidity level of the concentrated white liquor, of 30 for 25%. This loss in the sulfidity was not possible to be corrected through the addition of elementary sulfur in the system, due to limitations of the manufacturing sulfur solution system. The reduction of the sulfidity turned necessary the addition of salt cake in the tank of dust dilution of the recovery boiler. However, aiming at to reduce expenses with salt cake, a solution of sodium sesquisulfate became dosed in the tank of concentrated white liquor. Sodium sesquisulfate is a sub-product of the generating plant of chlorine dioxide.

Conclusions

This study evaluated the acid stage industrial implementation in the VCP-Jacareí Mill, converting the OOZ(DQ)(PO) sequence in the (OO)AZD(PO). This industrial implementation of the acid stage generated results that provide to the following conclusions:

- the acid stage reduced the kappa number in about 3 units;
- the efficiency of the ozone stage reduced significantly after the implementation of the acid stage;
- the formation of calcium oxalate scaling during ozone stage, was reduced;
- the filtrate of the bleaching plant coming back for the digester wash liquor tank storage, it elevated the contents of calcium, magnesium, iron and manganese;

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