

RAFAEL IGNACIO QUEZADA REYES

**ULTRAFILTRAÇÃO E ELETROCOAGULAÇÃO DE FILTRADOS DO  
BRANQUEAMENTO DE UMA FÁBRICA DE POLPA CELULÓSICA KRAFT  
PARA FINS DE REUSO**

Tese apresentada à Universidade Federal  
de Viçosa, como parte das exigências do  
Programa de Pós-Graduação em Ciência  
Florestal, para obtenção do título de *Doctor  
Scientiae*.

VIÇOSA  
MINAS GERAIS – BRASIL  
2017

**Ficha catalográfica preparada pela Biblioteca Central da  
Universidade Federal de Viçosa - Campus Viçosa**

T

Q59u  
2017

Quezada Reyes, Rafael Ignacio, 1982-  
Ultrafiltração e eletrocoagulação de filtrados do branqueamento  
de uma fábrica de polpa celulósica kraft para fins de reuso / Rafael  
Ignacio Quezada Reyes. - Viçosa, MG, 2017.  
viii, 62f. : il. (algumas color.) ; 29 cm.

Inclui anexos.

Orientador: Cláudio Mudadu Silva.

Tese (doutorado) - Universidade Federal de Viçosa.

Inclui bibliografia.

1. Polpação alcalina. 2. Polpa de madeira - Branqueamento. 3.  
Águas residuais - Purificação. I. Universidade Federal de Viçosa.  
Departamento de Engenharia Florestal. Programa de Pós-graduação em  
Ciência Florestal. II. Título.


CDD 22 ed. 634.98611

RAFAEL IGNACIO QUEZADA REYES

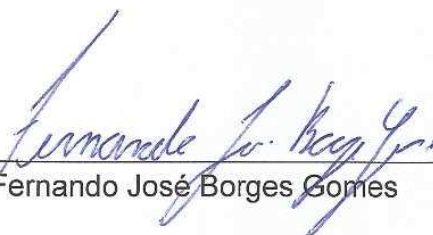
**ULTRAFILTRAÇÃO E ELETROCOAGULAÇÃO DE FILTRADOS DO  
BRANQUEAMENTO DE UMA FÁBRICA DE POLPA CELULÓSICA KRAFT  
PARA FINS DE REÚSO**

Tese apresentada à Universidade Federal de Viçosa, como parte das exigências do Programa de Pós-Graduação em Ciência Florestal, para obtenção do título de *Doctor Scientiae*.

APROVADA: 27 de julho de 2017.

  
Jorge Luiz Colodette

  
Regina Célia Santos Mendonça

  
Fernando José Borges Gomes

  
Ana Augusta Passos Rezende

  
Claudio Mudadu Silva  
(Orientador)

## AGRADECIMENTOS

À minha esposa Daniela, pelo amor, carinho, apoio e incentivo.

À minha mãe, Luisa Reyes e ao meu irmão Gonzalo Quezada pelo apoio, incentivo e por sempre acreditarem em mim.

Ao professor Claudio Mudadu Silva pela orientação, pelo incentivo e principalmente pela amizade.

À Celulosa Arauco e Constitución pelo apoio e suporte financeiro, em especial a Eduardo Rodriguez.

Aos professores Rubens Chaves de Oliveira, José Lívio Gomide, *in memoriam*, e Jorge Luiz Colodette, pelos ensinamentos e pelo incentivo durante o curso.

À Universidade Federal de Viçosa (UFV), e ao Departamento de Engenharia Florestal (DEF) pela oportunidade de realizar o doutorado.

À professora Regina Mendonça e a Paulina Mendoza pelo fornecimento do reator de eletrocoagulação e pela ajuda que muito contribuíram no desenvolvimento deste trabalho de tese.

À Marcio Neto pela ajuda no desenvolvimento do simulador.

Aos funcionários e amigos do Laboratório de Celulose e Papel, pelo apoio, amizade e atenção dispensada na realização desta tese.

Enfim, agradeço a todos que participaram desta vitória.

## SUMÁRIO

RESUMO.....	v
ABSTRACT .....	vii
INTRODUÇÃO GERAL.....	1
CAPITULO 1: Reuse of ultrafiltration membrane permeate and retentate of (EPO) filtrates from a kraft pulp mill bleaching plant .....	6
ABSTRACT .....	6
INTRODUCTION .....	6
MATERIAL AND METHODS .....	8
UF Membrane treatment.....	8
Membrane permeate reuse .....	9
Membrane retentate recycling .....	9
RESULTS AND DISCUSSION.....	10
UF Membrane treatment.....	10
Membrane permeate reuse .....	11
Membrane retentate recycling .....	13
CONCLUSIONS .....	15
ACKNOWLEDGMENTS .....	15
REFERENCES .....	15
CAPITULO 2: Ultrafiltration of acidic effluent from a kraft pulp mill.....	18
ABSTRACT .....	18
INTRODUCTION .....	18
MATERIAL AND METHODS .....	21
Effluent.....	21
UF membrane treatment.....	22
Membrane permeate reuse .....	23
Effects on the Effluent Treatment Plant (ETP) .....	23
RESULTS AND DISCUSSION.....	25

UF membrane treatment.....	25
Membrane permeate reuse .....	26
Effects on the ETP .....	28
CONCLUSIONS .....	29
ACKNOWLEDGMENTS .....	30
REFERENCES .....	30
CAPITULO 3: Treatment of bleaching PLANT effluent from a kraft pulp mill by Electrocoagulation process.....	34
ABSTRACT .....	34
INTRODUCTION .....	34
MATERIAL AND METHODS .....	36
Effluent.....	36
Electrocoagulation .....	37
Process simulation .....	38
Effects on the Effluent Treatment Plant (ETP) .....	39
RESULTS AND DISCUSSION.....	40
Effluent characterization .....	40
Electrocoagulation of acidic effluent.....	40
Electrocoagulation of alkaline effluent.....	43
Process simulation and clean water reuse.....	45
Effects on the Effluent Treatment Plant (ETP) .....	46
CONCLUSIONS .....	47
ACKNOWLEDGMENTS .....	48
REFERENCES .....	48
CONCLUSÕES GERAIS .....	52
ANEXO A .....	53
ANEXO B .....	60

## RESUMO

REYES, Rafael Ignacio Quezada, D.Sc., Universidade Federal de Viçosa, julho de 2017. **Ultrafiltração e electrocoagulação de filtrados do branqueamento de uma fábrica de polpa celulósica kraft para fins de reúso.** Orientador: Claudio Mudadu Silva.

Devido ao contínuo aumento das restrições ambientais em fábricas produtoras de polpa celulósica, a indústria tem procurado encontrar opções para minimizar o consumo de água, aumentar o reúso da água e melhorar a qualidade do efluente final. O tratamento de correntes líquidas setoriais da fábrica pode ser uma alternativa técnica e economicamente atrativa por possuírem baixos volumes e altas concentrações quando comparados ao efluente final que consiste na mistura de todos os efluentes da fábrica. Em estudos anteriores, foi determinada a viabilidade de utilizar ultrafiltração para o tratamento do efluente alcalino do setor de branqueamento da fábrica. O primeiro objetivo desse estudo foi avaliar o reúso do permeado gerado e a disposição do concentrado no ciclo de recuperação química. Os resultados indicaram que é possível substituir 100% da água quente na prensa (EPO) sem gerar incrustações de carbonato de cálcio e hidróxido de magnésio. De acordo com a caracterização do concentrado, estima-se que é possível a disposição do concentrado na área de evaporadores sem aumentar o risco de formação de incrustações ou afetar o funcionamento da caldeira de recuperação. O segundo objetivo foi determinar a viabilidade técnica de tratar o efluente ácido do setor de branqueamento com membranas de ultrafiltração e avaliar mediante simulações por software a viabilidade de reusar o permeado, a formação de incrustações de sulfato de bário e os efeitos na estação de tratamento de efluentes da fábrica. Os resultados indicaram que é possível tratar o filtrado ácido com membranas de ultrafiltração, a remoção de matéria orgânica e cor foi de 65% e 82% respectivamente. A simulação por software indicou que a substituição de 25% da água branca na prensa do primeiro estágio D pelo permeado, aumenta em 10% o risco de formação de incrustações de sulfato de bário. Neste caso o efluente final da fábrica possuiria uma carga de DQO 38% menor e a geração de lodo biológico diminuiria em 40%. O terceiro objetivo foi avaliar o tratamento de eletrocoagulação com eletrodos de ferro e alumínio, dos efluentes ácido e alcalino, determinar a viabilidade técnica de reusar os efluentes tratados e determinar os efeitos na estação de tratamento de efluentes (ETE). Os resultados indicaram que tanto para o efluente ácido

como para o efluente alcalino, a maior remoção de DQO foi obtida com o tratamento de eletrocoagulação com eletrodos de alumínio, 51% e 48% respectivamente. Pelas características finais dos efluentes tratados, conclui-se que os mesmos podem substituir a água quente na prensa (EPO) sem aumentar o risco de formação de incrustações de carbonato de cálcio. A substituição da água quente pelo efluente tratado diminui o consumo de água em 7,5 m<sup>3</sup> por tonelada de polpa seca.



## ABSTRACT

REYES, Rafael Ignacio Quezada, D.Sc., Universidade Federal de Viçosa, July, 2017. **Ultrafiltration and electrocoagulation of bleaching filtrates from a kraft pulp mill for reuse purposes.** Adviser: Claudio Mudadu Silva.

Due to the continuous rise of environmental concern of the pulp industry, it is necessary to find options that minimize the water consumption, and enhance effluent quality. The treatment of specific in-plant stream seems to be an attractive technical and economical approach because of the smaller amount of effluent to be treated compared with the total final effluent volume. Previous studies have shown that it is possible to treat alkaline extraction (EPO) effluent with ultrafiltration membranes. The first objective of this study was to evaluate the reuse of the ultrafiltration (UF) permeate and the transfer of the retentate to the chemical recovery cycle. The results showed that it was possible to replace 100% of the hot water in the (EPO)-press without generating scaling of calcium carbonate or magnesium hydroxide. According to the characteristics of the retentate, it is assumed that it is possible to transfer the UF-retentate to the evaporator area without increasing the risk of fouling or negatively affecting the operation of the recovery boiler. The second objective was to evaluate the feasibility of the bleaching plant acidic effluent ultrafiltration membrane treatment and study, using software simulations, the feasibility of reusing the permeate determining the risk of barium sulfate scaling and the effects on the final effluent treatment plant. The results indicated that it was possible to treat the acidic effluent with UF membranes, the removal of COD and color was 65% and 82%, respectively. Software simulation indicated that the 25% replacement of white water in the first D-stage press would increase by 10% the risk of barium sulfate formation. The final total effluent of the mill decreased by 38% of the COD load and the biological sludge generation decreased by 40%. The third objective was evaluating the electrocoagulation treatment with iron and aluminum electrodes of acidic and alkaline bleaching plant effluents, to determine the technical feasibility of reusing the treated effluents and to determine the effects on the effluent treatment plant. The results indicated that for both, acidic and alkaline effluent, the highest COD removal was achieved with the electrocoagulation treatment with aluminium electrodes, 51% and 48%, respectively. Due to the pH and

composition of the treated effluents, both treated effluents could replace hot water in the (EPO) press without increasing the risk of calcium carbonate scale formation. The substitution of hot water by treated effluent reduced water consumption by  $7.5 \text{ m}^3 / \text{ADt}$ .

## INTRODUÇÃO GERAL

O setor produtivo de polpa celulósica e papel consome um alto volume de água e devido ao constante aumento de sua demanda está perto de se transformar em um bem limitado em alguns países. A diminuição na disponibilidade da água gerou necessidade de redução do seu consumo através de práticas de controle preventivo da poluição pela modificação dos processos fabris.

O elevado consumo de água em processos industriais representa um grande problema para a indústria de polpa celulósica e papel, principalmente pelo elevado custo do tratamento dos efluentes gerados e tamanho dos equipamentos a serem utilizados (THOMPSON et al., 2001). Existem duas maneiras de resolver este problema: o tratamento geral destes efluentes, chamado de “tratamento de fim de tubo” ou, reduzir ou eliminar a geração na fonte, pelo procedimento de minimização do consumo de água através do reúso de correntes internas.

Em circuitos fechados, onde é realizado intenso reúso da água, diversos elementos químicos, denominados de elementos não-processáveis (ENP), são acumulados até atingir níveis de saturação no meio, podendo originar sérios problemas no processo e prejudicar a qualidade do produto final. As consequências mais comuns são a perda da qualidade da polpa branqueada, devido à presença de depósitos e entupimento de equipamentos e tubulações, com a consequente perda de eficiência do processo produtivo (SAIF et al., 2013; HUBER et al., 2014).

Tendências no tratamento de efluentes industriais, indicam que é mais adequado e conveniente, a implementação de medidas de tratamento em correntes líquidas internas da fábrica antes que elas sejam reutilizadas. As principais vantagens desta estratégia é a redução do volume do efluente a ser tratado e o menor tamanho dos equipamentos a serem utilizados, por conseguinte, menores custos de tratamento (BERUBE & HALL, 2000; KOSSAR, 2013; QUEZADA et al., 2014).

O branqueamento da polpa celulósica é a etapa, dentro do processo de fabricação de polpa Kraft, que gera o maior volume de efluentes. Uma sequência de branqueamento de polpa Kraft de eucalipto comumente utilizada tem sido D(EPO)DD, ou seja, um estágio com dióxido de cloro (D) seguido por extração

alcalina reforçada com peróxido de hidrogênio e oxigênio (EPO), seguido por outros dois estágios com dióxido de cloro.

Existem várias técnicas testadas para tratar o efluente gerado no branqueamento da polpa kraft (SEMPERE et al., 2002; MOUNTEER et al., 2007; QUEZADA et al., 2014). Nos últimos anos as tecnologias eletroquímicas, tais como eletrocoagulação, eletroflotação e eletrooxidação, tem sido utilizadas para o tratamento de efluentes (CHEN, 2004; VALENTE et al., 2012; PULKKA et al., 2014). Entre esses métodos, se destaca a eletrocoagulação como uma técnica promissora devido às suas características únicas: elevada degradação de poluentes, menor geração de lodo e facilidade na operação (ZAIED & BELLAKHAL, 2009; SRIDHAR et al., 2011).

Por outro lado, há alguns anos, tem-se empregado a tecnologia de filtração com membranas para o tratamento da água e/ou águas residuais. Atualmente, essa tecnologia é aplicada e se mostra viável para o tratamento de diferentes tipos de efluentes. A filtração por membranas pode ser classificada dependendo do diâmetro médio dos poros como: microfiltração (MF) ( 10 – 100  $\mu\text{m}$ ), ultrafiltração (UF) (2 - 100 nm), nanofiltração (NF) (500 - 2.000 g/mol) e osmose inversa (OI) ( <500 g/mol) (MÄNTTÄRI et al.,; KASHER, 2009; MURO, 2012; QUEZADA et al., 2014).

Existem programas de simulação de processos industriais que realizam balanços de massa bastante próximos dos processos industriais. Dentre esses programas, destaca-se o WinGEMS, largamente utilizado para simulações de unidades do processo de produção de polpa celulósica e papel (DIONÍSIO et al., 2010). O software WinGEMS não tem capacidade de realizar cálculos de formação de incrustações, dado importante para definir estratégias de reúso de efluentes. Para determinar o potencial de formação de incrustações diversos pesquisadores incorporam os modelos cinéticos de formação de sais ao software (LITVAY et al., 2003; WADSBORN, 2011; WADSBORN & RÅDESTROM, 2011).

O objetivo geral deste estudo foi avaliar o uso de membranas de ultrafiltração da eletrocoagulação no tratamento de efluentes gerados no branqueamento da polpa celulósica Kraft.

O primeiro capítulo trata do reúso do permeado do tratamento de ultrafiltração do efluente alcalino do setor de branqueamento e o envio do concentrado no ciclo de recuperação química.

O segundo capítulo trata do tratamento do filtrado ácido com membranas de ultrafiltração, o reúso do permeado dentro do setor de branqueamento e os efeitos na estação de tratamento de efluentes (ETE).

O terceiro capítulo aborda o tratamento de electrocoagulação com eletrodos de ferro e alumínio dos efluentes ácido e alcalino, o reúso do efluente tratado e os efeitos na ETE.

## REFERENCIAS

CHEN, G. Electrochemical technologies in wastewater treatment. **Separation and Purification Technology**, v. 38, n. 1, p. 11–41, 2004.

DIONÍSIO, K.; CARDOSO, M.; NICOLATO, R. Process simulation for water consumption minimization in pulp mill. **Latin American Applied Research**, v. 40, n. 1, p. 81–90, 2010.

HART, P. W. Kraft ECF pulp bleaching: A review of the and justify capital expenditures. **Tappi journal**, v. 12, n. 10, p. 19–29, 2013.

HUBER, P.; BURNET, A. A.; PETIT-CONIL, M. Scale deposits in kraft pulp bleach plants with reduced water consumption: a review. **Journal of Environmental Management**, v. 141, p. 36–50, 2014.

KASHER, R. Membrane-based water treatment technologies: Recent achievements, and new challenges for a chemist. **Bulletin of the Israel Chemical Society**, n. 24, p. 10–18, 2009.

KOSSAR, M. J. Proposal for water reuse in the Kraft pulp and paper industry. **Water Practice & Technology**, v. 8, n. 3–4, p. 359–374, 2013.

LITVAY, C.; RUDIE, A.; HART, P. Use of Excel ion exchange equilibrium solver with WinGEMS to model and predict NPE distribution in the Mead/Westvaco Evandale, TX, hardwood bleach plant. In: Proceeding of the 2003 TAPPI Fall Technical Conference, Chicago. **Anais...** Chicago: TAPPI Press, 2003.

MÄNTTÄRI, M.; PIHLAJAMÄKI, A.; NYSTRÖM, M. Comparison of nanofiltration and tight ultrafiltration membranes in the filtration of paper mill process water. **Desalination**, v. 49, 2002.

MOUNTEER, A. H.; PEREIRA, R. O.; MORAIS, A. A.; RUAS, D. B.; SILVEIRA, D. S. A.; VIANA, D. B.; MEDEIROS, R. C. Advanced oxidation of bleached eucalypt kraft pulp mill effluent. In: **Water Science and Technology**, 1999, Anais...2007.

PULKKA, S.; MARTIKAINEN, M.; BHATNAGAR, A.; SILLANPÄÄ, M. Electrochemical methods for the removal of anionic contaminants from water – A review. **Separation and Purification Technology**, v. 132, p. 252–271, 2014.

QUEZADA, R.; SILVA, C. M.; PASSOS REZENDE, A. A.; NILSSON, L.; MANFREDI, M. Membrane treatment of the bleaching plant (EPO) filtrate of a kraft pulp mill. **Water Science and Technology**, v. 70, n. 5, p. 843–50, 2014.

SAIF, Y.; ALMANSOORI, A.; ELKAMEL, A. Wastewater minimization in pulp and paper industries through energy-efficient reverse-osmosis membrane processes. **Chemical Engineering and Technology**, v. 36, n. 3, p. 419–425, 2013.

SEMPERE, A.; MEABE, E.; LOPETEGUI, J.; PÉREZ, F.; HERMOSILLA, D.; ORDÓÑEZ, R. Pulp & Paper industry Water Reuse by Ceramic membranes: Cost and ROI analysis. **Water**, 2002.

SILVA, C. M. O controle preventivo da poluição: efluentes industriais. **Ação Ambiental**, p.19-21, 2001.

SRIDHAR, R.; SIVAKUMAR, V.; PRINCE IMMANUEL, V.; PRAKASH MARAN, J. Treatment of pulp and paper industry bleaching effluent by electrocoagulant process. **Journal of hazardous materials**, v. 186, n. 2–3, p. 1495–502, 2011.

THOMPSON, G.; SWAIN, J.; KAY, M.; FORSTER, C. F. The treatment of pulp and paper mill effluent: A review. **Bioresource Technology**, v. 77, n. 3, p. 275–286, 2001.

VALENTE, G. F. S.; SANTOS MENDONÇA, R. C.; PEREIRA, J. A. M.; FELIX, L. B. The efficiency of electrocoagulation in treating wastewater from a dairy industry, Part I: Iron electrodes. **Journal of environmental science and health. Part. B, Pesticides, food contaminants, and agricultural wastes**, v. 47, n. 4, 2012.

WADSBORN, R. Modelling the scaling of burkeite Pitzer-formalism into WinGEMS. 2011.

WADSBORN, R.; RÅDESTROM, R. Metal ion distribution in a bleach plant - validation of chemical equilibrium calculations in WinGEMS. 2011.

ZAIED, M.; BELLAKHAL, N. Electrocoagulation treatment of black liquor from paper industry. **Journal of Hazardous Materials**, v. 163, n. 2–3, p. 995–1000, 2009.

## **CAPITULO 1: REUSE OF ULTRAFILTRATION MEMBRANE PERMEATE AND RETENTATE OF (EPO) FILTRATES FROM A KRAFT PULP MILL BLEACHING PLANT**

Artigo publicado: Journal of the Technical Association of the Australian and New Zealand Pulp and Paper Industry (APPITA). v.68, n.4, p.12-17, dezembro 2015.

### **ABSTRACT**

An oxygen- and peroxide-reinforced extraction stage (EPO) filtrate from a kraft pulp mill bleach plant was treated using an ultrafiltration (UF) membrane separation process that generates a permeate stream and a retentate stream. The feasibility of the UF permeate reuse in an (EPO) washing press was evaluated. According to the WinGEMS steady-state software simulation, 100% replacement of hot water with permeate was possible without critical accumulation of non-process elements (NPE) or  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$  scaling formation during the softwood and hardwood campaigns. The feasibility of membrane retentate reuse in the black-liquor recovery cycle (prior to evaporation) was also evaluated. The results showed a negligible increase in the load of critical elements in the weak black liquor. Therefore, no scaling formation or negative effect on the performance of the recovery boiler is expected.

*Keywords: (EPO) effluent, membrane treatment, pulp mill effluent, simulation, ultrafiltration, water reuse.*

### **INTRODUCTION**

The pulp and paper industry is the largest consumer of water among the industrial activities of the countries in the Organization for Economic Co-operation and Development (OECD). Since 1980, water pollution from the pulp and paper sector has been significantly reduced in most OECD paper-producing countries. Pulp mills all over the world have been required to develop ways to minimize water consumption and effluent discharges. The reuse of in-plant liquid streams is a logical alternative to be considered (DIONÍSIO et al., 2010) and the bleach plant is the major source of liquid effluent in modern mills (DENCE & REEVE, 1996). Bleach plant filtrate requiring external treatment is in the range of 15-30



m<sup>3</sup>/ADt (air dried tone of pulp). It is rich in organic matter and has a high color content and normally consists of two separate streams: an acidic stream and an alkaline stream. The alkaline filtrate has a high content of dissolved organic substances, measured by the COD (Chemical Oxygen Demand) and color, and this contributes significantly to the effluent quality of the entire mill (POKHREL; VIRARAGHAVAN, 2004).

Membrane filtration technology has been used in several industries, e.g., food, pharmaceutical, and water treatment (ROSENBERG et al., 2009; CHHAYA et al., 2013) and its use is increasing because new materials, better configurations, and cost reductions are rapidly developing. For example, until recently there was no polymeric membrane separation system that could resist high pH and temperature (KASHER, 2009). While membrane technology remains rarely used in Kraft pulp mills, there is an increased interest from the pulp industry to find technically and economically attractive options to reduce water consumption and minimize effluent generation. One notable example is a membrane filtration plant that has been in operation since 1995 to clean bleach plant effluent at a Swedish sulfite pulp mill (NORDIN & JÖNSSON, 2006). In that case, a suitable membrane type and configuration were selected for membrane treatment of alkaline (EPO) filtrates (pH 11 and temperature 70 °C) from a softwood and hardwood kraft pulp mill. Technically and economically optimal operation conditions for the system (transmembrane pressure, cross flow velocity, volume concentration factor and cleaning regime) to remove organic contaminants were selected. The results of this study showed that an ultrafiltration (UF) membrane with the pore size of 4000 g/mol achieved a COD and color removal of 65% and 93%, respectively (QUEZADA et al., 2014).

During membrane filtration, two streams are generated: a permeate stream and a retentate. To develop a water conservation program in a mill, the challenge is to reuse these streams without compromising the mill processes and the product quality. The accumulation of elements and compounds (non-process elements) in the water cycle can cause severe problems in the mill (ULMGREN, 1997; DOLDÁN et al., 2011), the most common in the bleach plant being associated with formation of barium sulfate, calcium carbonate and calcium oxalate. The amount of filtrate that can be reused depends on specific mill processes and configurations.

To predict the accumulation of non-process elements and the relative solubility of some compounds, it is possible to simulate these phenomena using computer simulation software (ULMGREN, 2001). The objectives of this study were to use pilot scale filtration and software simulation to evaluate the feasibility of recycling the UF permeate in the bleach plant and the reuse of the UF retentate in the black-liquor evaporation plant.

## **MATERIAL AND METHODS**

### **UF Membrane treatment**

A filtrate from the wash press after the oxygen- and peroxide-reinforced extraction stage (EPO) was obtained from a kraft pulp mill, where the wood type changed every 6 months from hardwood to softwood. In both campaigns, the bleaching sequence was D(EPO)DD.

A pilot membrane treatment of 19 L/min of (EPO) filtrate was performed during two months for each campaign (Figure 1). A continuous-feed two-stage membrane pilot plant was used. Each stage had three parallel tubular membrane modules, each of which was 3.6 m long and 1.3 cm in diameter, with a molecular weight cut-off of 4000 g/mol, and contained 18 perforated stainless-steel tubes in the form of a shell and a tube. Each tube was fitted with a membrane element. The operation conditions were a cross-flow velocity (CFV) of 3 m/s and a transmembrane pressure (TMP) of 7 bar, which provided a concentration volume factor (CVF) of 98. The membrane permeates and retentates obtained in both campaigns were collected, stored at 4°C, and characterized according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005). The parameters measured in the permeate and retentate were COD, pH, color, sodium, calcium, potassium, magnesium, manganese, barium, aluminum, sulfate, phosphorus and chloride. There were 15 repetitions of COD, pH, and color and 2 repetitions of the other parameters.

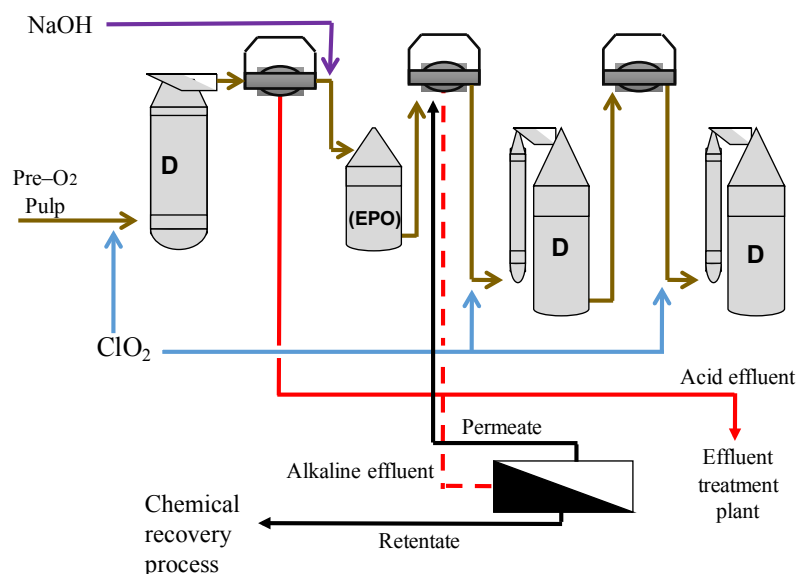


Figure 1 - Flowchart of the bleaching area with membrane treatment

### Membrane permeate reuse

A full mill model was developed in WinGEMS software, which specially focused on pulp and paper production. A steady-state model was created for the full pulp mill, including balances for water, energy, sodium/sulfur and non-process elements (NPE). Precipitation and accumulation models regarding handling of NPE's and scaling was integrated into the software (ULMGREN, 1997, 2001). The model takes into account temperature, ionic strength, pH, concentrations, over-saturation etc. to predict the solubility for each compound and the extent to which precipitations may occur.

Using the simulation model, the hot fresh water added to the (EOP) press was stepwise replaced with permeate from the membrane filtration unit until 100% of the washing liquor on the press was the UF permeate. The simulations were run in each case to the steady-state condition after various recycle rates of the permeate, and the risk of the effects in the pulp mill was evaluated.

### Membrane retentate recycling

The small concentrated stream obtained from the UF treatment of the (EPO) filtrate was rich in organic matter with high molecular weight compounds. One possible alternative to reuse this stream was to send it to the black liquor cycle.

The effect of reusing the UF retentate fraction on the black-liquor evaporation plant was evaluated by comparing the concentration of specific elements in the weak black liquor (WBL) with the mixture of UF retentate (WBL) for each campaign. The elements and compounds that were assessed according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2005) in the retentate and the weak black liquor were: sodium, calcium, potassium, magnesium, manganese, barium, aluminum, silicon, phosphorus, chloride and sulfate. Two repetitions were performed for each parameter.

## RESULTS AND DISCUSSION

### UF Membrane treatment

The separation with ultrafiltration membrane achieved a 79% removal of the COD and 86% removal of the color. The results indicate that the permeate flow and the removal of COD and color did not change significantly by changing the raw material for the production of bleached pulp. The characterization of the (EPO) filtrate, UF permeate and UF retentate from the pilot filtration is shown in Table 1.

Table 1 - Characterization of the (EPO) filtrate, UF permeate and UF retentate

Parameter	Hardwood campaign			Softwood campaign			Hot water
	(EPO) filtrate	Permeate	Retentate	(EPO) filtrate	Permeate	Retentate	
Flow [L/s]	200	198	2	200	198	2	
Sodium [mg/L]	707	694	1630	679	666	1428	1.5
Calcium [mg/L]	8.5	1.36	51.0	2.6	0.95	59.9	1.6
Potassium [mg/L]	51.3	50.6	41.0	13.1	12.7	39.2	0.02
Magnesium [mg/L]	2.2	0.07	132	0.6	0.09	47.0	1.3
Manganese [mg/L]	0.10	n.d*	7.0	0.15	n.d*	21.7	0.02
Barium [mg/L]	0.07	0.005	0.12	0.02	0.01	0.39	0
Aluminum [mg/L]	0.20	0.14	32.0	0.26	0.2	30.5	0.05
Sulfate [mg/L]	250.0	163.7	248	n.d*	163.7	492	30
COD [mg/L]	1890 ± 150	380	n.d*	1600 ± 200	320	n.d*	0
pH	10	10	n.d*	10	10	n.d*	n.d*
Color [CU]	850 ± 120	120	n.d*	640 ± 110	90	n.d*	0
Temperature [°C]	70	n.d*	n.d*	70	n.d*	n.d*	n.d*

## Membrane permeate reuse

The calcium carbonate formation in the (EPO) filtrate can be a critical parameter causing operational problems in the bleach plant because of scaling, particularly on the pulp washers. In the softwood campaign, the calcium concentration was lower in the UF permeate (0.95 mg/L) than in the hot water (1.60 mg/L) and therefore it decreased when the UF permeate reuse increased. However, a much higher concentration of carbonate ions in the permeate (350 mg/L) compared to hot water (where it could not be detected) increased the formation of calcium carbonate in the (EPO) stage pulp and in the (EPO) filtrate (Figure 2).

In the (EPO) stage, the calcium carbonate formation increased with the addition of carbonate ions as calcium carbonate was precipitated and was trapped by the fibers.

Figure 2 shows that calcium carbonate formed in the (EPO) filtrate when UF permeate replacement of hot water reached 50%. However, the amount of calcium carbonate formed, even at 100% replacement of hot water was still below the supersaturation point (the concentration of calcium and carbonate necessary to start precipitation (WOJTOWICZ, 1998; DUGGIRALA, 2005). Even if extra permeate were to be added, to the extent that the supersaturation concentration was exceeded, the calcium carbonate retains calcium and carbonate ions in the solution, i.e., an initially even higher concentration than equilibrium is required to begin the precipitation of calcium carbonate. However, when the precipitation begins, all precipitates immediately form at that point (WOJTOWICZ, 1998).

The reuse of UF permeate increases the risk of precipitation compared to the base case, but according to these simulations, the risk is small.

The hardwood campaign had higher calcium carbonate levels in the fiber line than the softwood campaign, but no formation of calcium carbonate in the (EPO) filtrate was observed in the simulations. (Figure 3). According to analysis, there would be a slightly different split of calcium carbonate in the wash press with less calcium carbonate to filtrate and more calcium carbonate to the following bleaching stage. Note that the solubility data differ between hardwood and softwood.

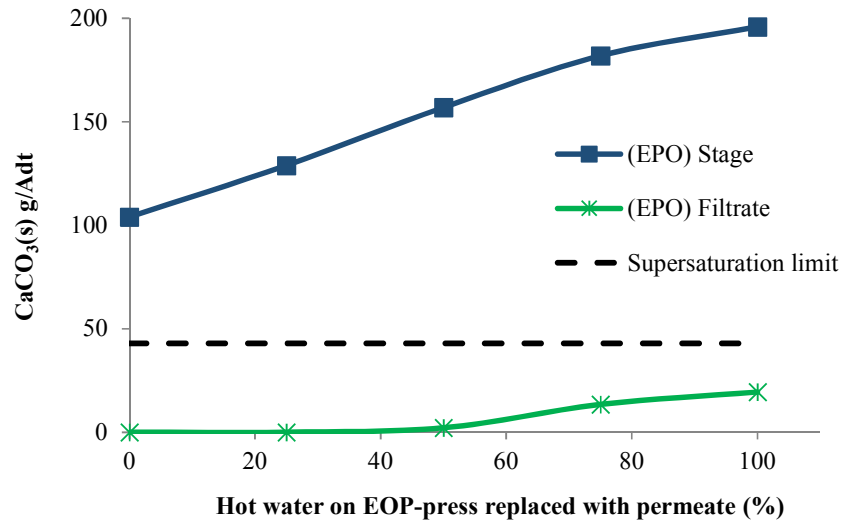


Figure 2 - Calcium carbonate formation in the (EPO) stage and filtrate during the softwood campaign with hot-water replacement.

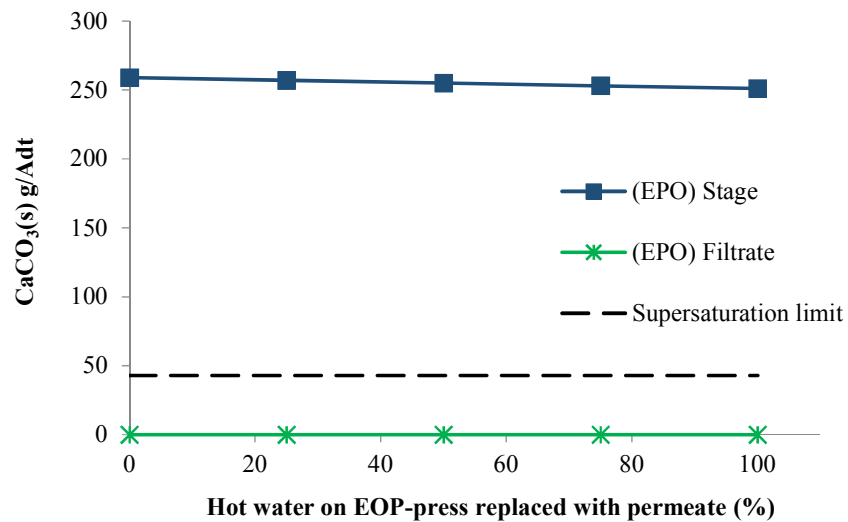


Figure 3 - Calcium carbonate formation in the (EPO) stage and filtrate during the hardwood campaign with hot-water replacement.

The magnesium hydroxide formation decreased in both campaigns in the (EPO) stage when the UF permeate use was increased because there was less magnesium in the UF permeate than in the hot water (Table 1). In the softwood campaign, the magnesium hydroxide formation was 185 g/Adt without using UF permeate and 160 g/Adt with 100% of UF permeate use. In the hardwood campaign, these values were 61 g/Adt and 50 g/Adt, respectively.

The recycling of 100% UF permeate reduced the water consumption of the bleaching area by 5.4 m<sup>3</sup>/ADt and 5.8 m<sup>3</sup>/ADt in the hardwood and softwood campaigns, respectively.

### **Membrane retentate recycling**

According to the flow and elemental composition of the membrane retentate, the addition of this stream into the weak black liquor prior to evaporation would result in a negligible increase in the concentration of the assessed elements in the weak black liquor (Table 2). During the hardwood campaign, the aluminum and manganese concentrations had the largest increase in the weak black liquor (1.72% and 1.96%, respectively). In the softwood campaign, aluminum and magnesium had the largest increase in concentration (2.63% and 2.59%, respectively).

WinGEMS simulation was performed for the softwood campaign. In the simulations, the retentate was added to the weak black liquor. This was done to fully study the build-up of non-process elements. The steady state results showed that the chloride levels in the black and white liquor would increase by 5%, assuming that the ESP-dust extraction rate is held constant. The need for make-up chemicals would decrease slightly due to the addition of sodium and sulfate. If a slightly higher ESP-dust extraction rate was to be applied to limit the increase in chloride levels, a slightly higher consumption of make-up chemicals should be expected.

Black liquor is composed of the organic material dissolved from the wood in the digester and from the oxygen delignification plant and also of cooking and oxygen-bleaching chemicals. In the recirculation of bleach plant effluent, the dissolved material from bleaching and chemicals used in bleaching are also found in the black liquor. In addition, non-process elements that circulate in the chemical recovery cycle are also found (CARDOSO et al., 2009).

Scaling on heat transfer surfaces occurs at high dry-solid concentration. The scaling tendency of the black liquor depends on the calcium content and the amount of inert components, such as sodium sulfate and sodium carbonate (CHEN & GAO, 2004). Calcium carbonate scaling in the evaporators is the most frequently identified inorganic-deposit in the kraft cycle. This phenomenon occurs in the presence of optimal substrate (non-uniform surface), optimal conditions (temperature shocks and alkaline pH) and increases in the concentrations of

dissolved cations and anions, such as calcium and carbonate (MACADAM & PARSONS, 2004). With the levels of chemicals in the membrane retentate and the black liquor, the simulation shows that the calcium concentration in the weak black-liquor stream should increase by 0.66% and 1.13% in softwood and hardwood campaigns, respectively. It is expected that this increase of the calcium concentration will not induce calcium carbonate scaling.

Table 2. Comparison of load factors between weak black liquor and the membrane retentate

Parameter	Hardwood campaign				Softwood campaign			
	Weak black liquor		Retentate	CI [%]	Weak black liquor		Retentate	CI [%]
	[mg/L]	[kg/h]			[mg/L]	[kg/h]		
Sodium	165600	26380	10.28	0.04	30900	35596	11.74	0.03
Calcium	410	65	0.43	0.66	29	33	0.37	1.13
Potassium	2270	361	0.28	0.08	2934	3379	0.29	0.01
Magnesium	160	25.5	0.34	1.33	32	36.6	0.95	2.59
Manganese	50	8.0	0.16	1.96	3.5	4.0	0.05	1.24
Barium	10	1.59	0.003	0.18	0.2	0.22	0.001	0.39
Aluminum	80	12.7	0.22	1.72	7.6	8.8	0.23	2.63
Silicon	479	76.3	0.11	0.14	35	40.2	0.34	0.84
Phosphorus	345	55.0	0.06	0.10	14	16.1	0.06	0.34
Chlorine	1502	239	0.83	0.35	500	576	1.25	0.22
Sulfate	46547	7415	3.55	0.05	3600	4147	1.79	0.04

CI= Concentration increment of the element on the weak black liquor after adding the (EPO) membrane retentate.

From the viewpoint of recovery boiler chemistry, the molar ratio between total sulfur and sodium in the black liquor, is one of the most important parameters. There is a critical relationship governing the chemistry of sulfur and sodium in the recovery boiler and it varies significantly among different processes and even in the same process depending on the operation strategy of the boiler (EMPIE, 2009).

Comparing the sodium and sulfate contents of the membrane retentate and the black liquor, sodium increased by 0.04% and 0.03%, whereas sulfur in the form of sulfate increased by 0.05% and 0.04% for softwood and hardwood, respectively. It is therefore expected that the ratio of sulfur/sodium will remain essentially unchanged after the retentate addition to the black liquor stream, and hence the recovery boiler chemical performance will not be affected.



## CONCLUSIONS

The membrane treatment obtained a COD removal of 79% and 86% of color.

In both hardwood and softwood cases, simulation predicts that 100% replacement of hot water in the (EPO) press should be technically possible (saving 5.4 m<sup>3</sup>/ADt and 5.8 m<sup>3</sup>/ADt, respectively). All precipitation levels slightly decreased because of the lower NPE content in the permeate, and the supersaturation calculations indicate that the precipitation of calcium carbonate will not start even with 100% of the hot water being replaced by UF permeate.

According to the characterization of the (EPO) retentate, it should be feasible to recycle the retentate to the evaporation area without scaling formation or affecting the performance of the recovery boiler.

## ACKNOWLEDGMENTS

We would like to thank the Universidade Federal de Viçosa, the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) for the financial support and the Estudantes-Convênio de Pós-Graduação program – PEC-PG, of CAPES/CNPq - Brazil

## REFERENCES

CARDOSO, M.; DE OLIVEIRA, É. D.; PASSOS, M. L. Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills. **Fuel**, v. 88, n. 4, p. 756–763, 2009.

CHEN, F. C.; GAO, Z. An analysis of black liquor falling film evaporation. **International Journal of Heat and Mass Transfer**, v. 47, n. 8–9, p. 1657–1671, 2004.

CHHAYA; MAJUMDAR, G. C.; DE, S. Primary Clarification of Stevia Extract: A Comparison Between Centrifugation and Microfiltration. **Separation Science and Technology**, v. 48, n. 1, p. 113–121, 2013.

DENCE, C.; REEVE, D. W. Pulp Bleaching. Atlanta: **TAPPI Press**, 1996.

DIONÍSIO, K.; CARDOSO, M.; NICOLATO, R. Process simulation for water consumption minimization in pulp mill. **Latin American Applied Research**, v. 40, n. 1, p. 81–90, 2010.

DOLDÁN, J.; POUKKA, O.; SALMENOJA, K.; BATTEGAZZORE, M.; FERNANDEZ, V.; ELUÉN, I. Evaluation of sources and routes of non-process elements in a modern eucalyptus kraft pulp mill. **O Papel**, v. 72, n. 7, p. 47–52, 2011.

DUGGIRALA, P. Formation of calcium carbonate scale and control strategies in continuous digesters. CD del II Coloquio Internacional sobre Celulosa, 2005.

EATON, A.D.; CLESCERI, L.S.; RICE, E.W.; GREENBERG, A.E.; Standard Methods for the Examination of Water & Wastewater. **Ed. 21, American Public Health Association USA (APHA)**, 2005.

EMPIE, H. Fundamentals of the kraft recovery process. **TAPPI Press**, 2009.

KASHER, R. Membrane-based water treatment technologies: Recent achievements, and new challenges for a chemist. **Bulletin of the Israel Chemical Society**, n. 24, p. 10–18, 2009.

MACADAM, J.; PARSONS, S. A. Calcium carbonate scale formation and control. **Reviews in Environmental Science and Biotechnology**, v. 3, n. 2, p. 159–169, 2004.

MILESTONE, C. B.; ORREGO, R.; SCOTT, P. D.; WAYE, A.; KOHLI, J.; KOVACS, T.; HEID FURLEY, T.; SLADE, A. H.; HOLDWAY, D.; HEWITT, L. M. Evaluating the potential of effluents and wood feedstocks from pulp and paper mills in Brazil, Canada, and New Zealand to affect fish reproduction: chemical profiling and in vitro assessments. **Environmental science & technology**, v. 46, n. 3, p. 1849–58, 2012.

NORDIN, A. K.; JÖNSSON, A. S. Case study of an ultrafiltration plant treating bleach plant effluent from a pulp and paper mill. **Desalination**, v. 201, n. 1–3, p. 277–289, 2006.

POKHREL, D.; VIRARAGHAVAN, T. Treatment of pulp and paper mill wastewater--a review. **The Science of the total environment**, v. 333, n. 1–3, p. 37–58, 2004.

QUEZADA, R.; SILVA, C. M.; PASSOS REZENDE, A. A.; NILSSON, L.; MANFREDI, M. Membrane treatment of the bleaching plant (EPO) filtrate of a kraft pulp mill. **Water science and technology**, v. 70, n. 5, p. 843–50, 2014.

ROSENBERG, E.; HEPBILDIKLER, S.; KUHNE, W.; WINTER, G. Ultrafiltration concentration of monoclonal antibody solutions: Development of an optimized method minimizing aggregation. **Journal of Membrane Science**, v. 342, n. 1–2, p. 50–59, 2009.

ULMGREN. Non-process elements in a bleached kraft pulp mill with a high degree of system closure - state of the art. **Nordic Pulp and Paper Research Journal**, v. 12, n. 1, p. 032–041, 1997.

ULMGREN. A steady state model describing the solubility of calcium oxalate in D(chlorine dioxide stage)-filtrates. **Nordic Pulp and Paper Research Journal**, v. 16, n. 4, p. 389–395, 2001.

WOJTOWICZ, J. Factors affecting precipitation of calcium carbonate. **J. Swimming Pool Spa Ind**, v. 3, n. 1, p. 18–23, 1998.

## **CAPITULO 2: ULTRAFILTRATION OF ACIDIC EFFLUENT FROM A KRAFT PULP MILL**

### **ABSTRACT**

The objective of this study was to evaluate the use of membrane technology to treat chlorine dioxide stage acidic effluent from a kraft pulp mill bleach plant. A pilot plant using ultrafiltration (UF) membranes with an average pore size of 4.000 g/mol was used to determine the feasibility of the treatment. The reuse of the permeate and the effects on the effluent treatment plant (ETP) were evaluated using the simulation softwares, WinGEMS™ and BioWin™. The acidic effluent ultrafiltration achieved a COD and color removal of 65% and 82%, respectively. If the permeate is reused within the bleaching process, it is expected to increase the risk of scaling of barium sulfate in the first chlorine dioxide stage in 10% when 25% of the drier whitewater is replaced with permeate. In this scenario, software simulation results indicated a decrease in the COD of the final effluent and in the biological sludge generation in 42% and 37%, respectively.

*Keywords: Ultrafiltration, acidic effluent, bleaching, simulation process, water reuse.*

### **INTRODUCTION**

Due to the continuous increase in the environmental restrictions and public awareness, the pulp and paper industry is looking for options to reduce water consumption (BAJPAI, 2012). In a kraft pulp process, the removal of the residual lignin from the pulp suspension by means of chemical reactions is carried out in a bleaching plant. The bleaching process consists of several stages, in which the pulp is chemically treated and then washed to remove spent bleaching chemicals and dissolved pulp components (HUBER et al., 2014). After the first ClO<sub>2</sub> stage (D), an extraction stage is employed to dissolve soluble in alkali. In a modern bleaching sequence, the extraction stage is reinforced with oxygen and hydrogen peroxide (EPO), increasing the lignin removal and brightness (BRIAN N. & BROGDON, 2008).

In general, each bleaching stage is composed of a mixer reactor followed by a pulp washer. The bleaching plant filtrates from the washers constitute the major source of effluent that is sent to the effluent treatment plant (ETP).

The chemical composition of the bleaching filtrates depends greatly on the incoming wood raw material, the bleaching sequence and the precise condition under which the bleaching stages are performed.

A difference in the molecular weight distribution has been detected between the alkaline and acid effluent from an ECF (elemental chlorine free) plant (VAN TRAN, 2006). The alkaline filtrate contains a significantly higher proportion of high molecular weight substances (65-75%) than the acidic filtrate (20%). The lignin in the acidic filtrate has a much lower molecular weight than that in the alkaline effluent (DENCE & REEVE, 1996).

The treatment of specific in-plant streams seems to be an attractive technical and economical approach because it allows the use of advanced technologies such as membrane filtration (KASHER, 2009).

Several studies have reported the use of a membrane filtration to treat alkaline bleaching plant effluent (NORDIN & JÖNSSON, 2006; QUEZADA et al., 2014) ADICIONAR MAIS, but only few studies have evaluated the feasibility of the membrane treatment of the acidic effluent.

The characteristics of the effluent to be treated directly affect the selection of membrane. The factors that most affect polymeric membrane structure are the temperature and pH (NILSSON et al., 2008). Extremes pH can produce a dissociation of the functional groups of the membrane and may cause the pores to swell (LUO & WAN, 2013). The develop of new polymeric membrane material with better resistance to extreme conditions and with higher fluxes is useful for industrial applications (SHARMA, 2005)

By increasing water circuit closure of the bleach plant, some dissolved species can accumulate in process loops, which may lead to scale deposits. The most frequent types of scale in bleaching lines are composed of calcium carbonate (in the alkaline stages), calcium oxalate and barium sulfate (in the acidic stages). Barium sulfate (Barite) deposits form in supersaturated solutions containing both barium and sulfate. The main barium source is the wood (higher in the bark than in the stem) and the main sulfate source is the sulfuric acid used for pH regulation (HUBER et al., 2014). Barite ( $\text{BaSO}_4$ ) is a very insoluble mineral and it is less soluble at cold temperatures, so that it is important to avoid

temperature drops anywhere in the bleaching line, especially on the washers. The precipitation tendency of barite is pH-dependent; this is because the availability of sulfate anions is governed by the second dissociation of sulfuric acid. Barite does not require high supersaturation to start precipitating. Therefore, there is a risk of precipitation as soon as Saturation Index is higher than zero ( $SI > 0$ ). Although there is a limited amount of barium in wood (corresponding to a few mM concentration in the conditions of the bleaching line), any increase in the barium source may enhance barite deposits (RUDIE & HART, 2006).

Process simulation have proved to be very useful in designing and optimizing pulp and paper production processes. Various applications have been developed using some simulation packages: ASPEN Plus (OLSSON, 2009), CADSIM (DIONÍSIO et al., 2010), WinGEMS (CULBERTSON et al., 2016), and others.

WinGEMS (Metso Automation) is a process simulator developed for application in the pulp and paper industry. Steady-state and dynamic behavior can be modelled using this simulator, it is useful when calculating long-term trends, debottlenecking and performing economic analysis. Dynamic modelling can be used for storage analysis, developing control strategies or tracking component flow through the system and investigating build up times. The software uses a sequential modular approach in an interactive way for calculation of mass and energy balances. It has advantages for being relatively easy to learn and user-friendly. However, the basic version is rather limited, especially when it comes to more detailed process chemistry. The software, however, has the advantage of allowing the user to expand the capabilities by implementation of new calculation routines. WinGEMS only resolve mass and heat balances, but do not account for chemical equilibria. On the other hand, chemical speciation methods can help to determine local scaling risk in a given process, but do not help to predict the consequences of a process modification as such. To solve this problem, it is possible to create a bridge between process simulation and chemical speciation engines in order to take into account electrolyte chemistry problems.

The objectives of the present work were to evaluate i) the feasibility of the ultrafiltration membrane treatment of the bleach plant acidic effluent from a kraft pulp mill, ii) software simulation tool to simulate the feasibility to recycle the clean

filtrate and determine the risk of barium sulfate precipitation, and iii) evaluate the effects on the effluent treatment plant with software simulation.

## MATERIAL AND METHODS

### Effluent

The acidic bleach plant effluent (Table 1) was obtained from a softwood kraft pulp mill with a bleaching sequence  $D_0(EPO)D_1D_2$ . Three samples were obtained from the washpress after the first D-stage during normal operation. The COD, color and metals were determined according to Standard Methods for the Examination of Water and Wastewater (APHA, 2005).

In the mill, after each chlorine dioxide bleaching stage (D) the pulp was washed, the  $D_0$  stage pulp was washed with filtrate from the  $D_1$  press and the  $D_1$  pulp was washed with the  $D_2$  filtrate. The  $D_2$  pulp was washed with whitewater from the drainage of the pulp drying process. A characterization of the whitewater is also presented in Table 1.

Table 1 – Bleach plant acidic effluent characterization

Parameter (mg/L)	Acidic effluent	Whitewater
COD	$1650 \pm 31$	n.d*
Color	$755.4 \pm 16$	n.d*
Na	$170.16 \pm 13$	$162 \pm 7$
Ca	$14.12 \pm 1.3$	$3.22 \pm 0.5$
K	$15.32 \pm 1.8$	$0.6 \pm 0.1$
Mg	$1.68 \pm 0.12$	$0.5 \pm 0.1$
Mn	$0.31 \pm 0.03$	$0.03 \pm 0.01$
Ba	$0.06 \pm 0.01$	$0.01 \pm 0.01$
Al	$0.49 \pm 0.03$	$0.22 \pm 0.05$
Cu	$0.03 \pm 0.01$	n.d*
Si	$0.54 \pm 0.01$	$4.3 \pm 0.2$
P	$1.16 \pm 0.03$	n.d*
Fe	$0.36 \pm 0.01$	n.d*
SO <sub>4</sub>	$910 \pm 50$	$605 \pm 11$

\*n.d: not determined

## UF membrane treatment

The membrane treatment was carried out using a batch feed one-stage pilot plant (Figure 1). The pilot plant was equipped with 4 PCI B1 series flow module (tubular), with a single flow through the membrane (Figure 2). The membrane was 1.2 m long and 1.3 cm in diameter, the total membrane area per module was  $1.3 \times 10^{-5} \text{ m}^2$ .



Figure 1 – Ultrafiltration Pilot Plant

The feed pump has operated at a pressure of 6 bar. The pilot plant was fed with the acidic effluent previously collected, characterized and stored at 5°C.

The tubular membrane type used in this study (ESP04) was manufactured by PCI, made by modified polyether sulfone with a molecular weight cut-off (MWCO) of 4.000 g/mol. Three tests were carried out with 10 L of effluent each, until the maximum volumetric concentration factor (VCF) was achieved.

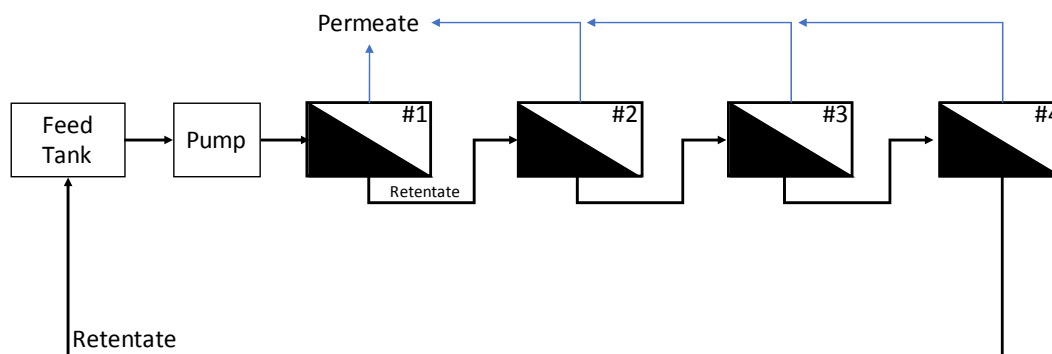


Figure 2 - Batch feed pilot plant scheme



## **Membrane permeate reuse**

The feasibility of the reuse of the UF-permeate in the bleaching area was studied by process simulation, in order to determine the risk of scaling formation of barium sulfate (barite).

The strategy of create a bridge between process simulation and chemical speciation engines in order to take into account electrolyte chemistry problems was adopted in this study: the basic WinGEMS version was expanded with the Pitzer electrolytic solutions model for calculation of chemical equilibrium. The Pitzer model takes as input the composition a given solution (in terms of molality, or moles of component per kg of solvent), as well as several thermodynamic parameters. As out-put, it calculates the activity coefficient of each component in solution. These activity coefficients are necessary for solubility calculations, as they are related to the solubility products  $K_{sp}$  of the precipitating electrolytes.

The new WinGEMS block was developed through the Block Development Kit (BDK) application-programming interface (API), specifically designed to allow users to create their own specialized blocks. BDK consists of a collection of static libraries, header and source C++ files that, when compiled into a dynamic-link library (DLL), provides the subroutines to be called by the custom block.

Using the simulation model, the whitewater added to the D<sub>2</sub> press was replaced with UF permeate. The simulations were run, in each case, to the steady-state condition at permeate reuse rates of 0%, 25%, 50% and 100%.

## **Effects on the Effluent Treatment Plant (ETP)**

The effects of the ultrafiltration of the acidic effluent on the effluent treatment plant was evaluated by process simulation in BioWin (EnviroSim) software. The final treated effluent characteristics and sludge production were determined.

The mill's effluent biological treatment plant consists of an activated sludge plant (Table 2). Each line is constituted by 4 biological selector reactors in series with 2.1, 1.7, 0.9 and 0.9 h of retention time) followed by one bioreactor (8.9 h of retention time) and a clarifier.

The readily biodegradable COD, non-colloidal slowly biodegradable COD, unbiodegradable soluble COD and unbiodegradable particulate COD were determined by respirometric and/or chemical methods. Five samples were

collected at the neutralization stage (before the biological treatment) and five to the treated effluent

The readily biodegradable COD was determined by respirometric and chemical methods. The respirometric method consist in adjust a sample from neutralization chamber to the relation food/microorganism (F/M) 0.3. The sample was saturated with oxygen to a concentration of 7 mg O<sub>2</sub>/L. When the aeration stopped, the amount of oxygen was measured every 2 minutes for 30 minutes. The specific oxygen uptake rate (SOUR) was obtained (slope of the graph dissolved oxygen vs time). The first fraction of the graph SOUR vs time presented the readily biodegradable COD.

The chemical method consists in a coagulation with Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> (100 mg/L) fallowed by a filtration (0,45 µm) of the samples from the neutralization stage and from the treated effluent. The COD from the coagulated and filtrated sample was the readily biodegradable and the non-biodegradable COD, the readily biodegradable was obtained subtracting the coagulated and filtrated treated effluent COD.

The COD measurement of all the fractions allows also determinate the non-colloidal slowly biodegradable COD (gCOD/f of slowly degradable COD), unbiodegradable soluble COD (gCOD/g of total COD), unbiodegradable particulate COD (gCOD/g of total COD), etc.

Table 2 – Biological treatment plant specifications

Parameter	Value
Lines	2
Hydraulic retention time (h)	14.5
Solids retention time (d)	15
Nitrogen source	Urea
Phosphorus source	Phosphoric acid
Total kjeldahl nitrogen dosage per line (kg/d)	311
Total Phosphorus dosage per line (kg/d)	90
Returned biosludge/Influent ratio	1

Table 3 – Inffluent characteristics

Parameter	Value
Total Flow (m <sup>3</sup> /d)	60000
Total COD (kg/d)	42600
Total COD (mg/L)	712
pH	7.3
Kjeldahl nitrogen (kg/d)	52
Phosphorus (kg/d)	58
Total suspended solids (kg/d)	8260

In order to determine sludge production and treated effluent characteristics, four scenarios were evaluated. Scenario 1: simulate the biological treatment of the current industrial effluent as a reference; Scenario 2: simulate the biological effluent treatment without the acidic filtrate but with the added UF permeate; Scenario 3: simulate the biological effluent treatment without the acidic filtrate and without the UF permeate (the permeate from the UF was recycled within the mill) and Scenario 4: Simulate the biological treatment without the acidic filtrate; and with 25% of replacement of white water on the bleaching plant.

## RESULTS AND DISCUSSION

### UF membrane treatment

According to commercial specification, the ESP04 ultrafiltration membrane have resistance to extremes pH and high temperature, this was confirmed by the results obtained. No irreversible fouling produced by the swelling of the pores was observed and COD and color reduction were achieved.

The characterization of the ultrafiltration permeate and retentate obtained in the pilot plant (Figure 2) is shown in Table 4. The treatment with ultrafiltration achieved a COD and color removal of 65% and 82%, respectively. It was possible to concentrate the effluent to a concentration factor (VCF) of 0.92, this means that for every 100 L/s treated, the stream of retentate should have a flow rate of 8 L/s.

The separation and concentration of heavy metals from wastewaters is a proven application of membrane technology (reverse osmosis) (COX, 2006; STOVER, 2012; SAIF; ALMANSOORI; ELKAMEL, 2013). Metal solubility varies

with pH, in a UF-based wastewater treatment system usually the pH is first raised to precipitate metals out of the solution and then the UF-treatment is carried.

Table 4 – Characterization of acidic filtrate and ultrafiltration resulting streams

Parameter	Acidic effluent	UF-Permeate	Reduction (%)	UF-Retentate
COD (mg/L)	1650 ± 45	581 ± 27	64.8	8121
Color (CU)	755 ± 31	139 ± 17	81.6	4511
Na (mg/L)	170.16 ± 7	143 ± 5	15.8	298
Ca (mg/L)	14.12 ± 0.5	11.45 ± 0.4	18.9	27.60
K (mg/L)	15.32 ± 0.3	12.24 ± 0.5	20.1	27.92
Mg (mg/L)	1.68 ± 0.1	1.44 ± 0.09	14.2	2.92
Mn (mg/L)	0.31 ± 0.01	0.25 ± 0.01	20.7	0.70
Ba (mg/L)	0.06 ± 0.01	0.057 ± 0.01	5.1	0.03
Al (mg/L)	0.49 ± 0.005	0.45 ± 0.007	8.5	0.75
Si (mg/L)	0.54 ± 0.02	0.20 ± 0.03	63.6	2.62
P (mg/L)	1.16 ± 0.02	1.00 ± 0.03	14.3	1.19
Fe (mg/L)	0.36 ± 0.01	0.39 ± 0.01	2.1	0.15
Cl (mg/L)	8.00 ± 0.6	7.01 ± 0.05	8.1	0.65

± Standard derivation

In this case, the pH of the acid filtrate was 3.4, so presumably the metals are in solution. According to the molecular weight cut-off of the ultrafiltration membrane the heavy metals should pass through the membrane and stay on the permeate fraction. The reduction of metals and inorganics by ultrafiltration was observed (Table 2). Silica had the highest removal (63%). Ca, K, Mn and P had a removal of 19, 20, 21, and 14%, respectively. It is reported that metals can be removed by the interaction with suspended solids, colloids or fiber (BERNAT et al., 2007; BERNATA et al., 2008; QIU & MAO, 2013).

In order to avoid scaling formation of Barite, is necessary to remove barium from the effluent, the UF treatment only removed 5%.

### Membrane permeate reuse

The barite (BaSO<sub>4</sub>) deposits formation in the D-stages can be a critical parameter causing operational problems in the bleach plant. The main source of

barium is the wood and the presence of sulfate is due to the use of sulfuric acid for pH regulation or as carry-over from brownstock washing (HUBER et al., 2014). Figure 3 shows the barite formation in acidic bleaching stages when the whitewater was replaced by UF permeate.

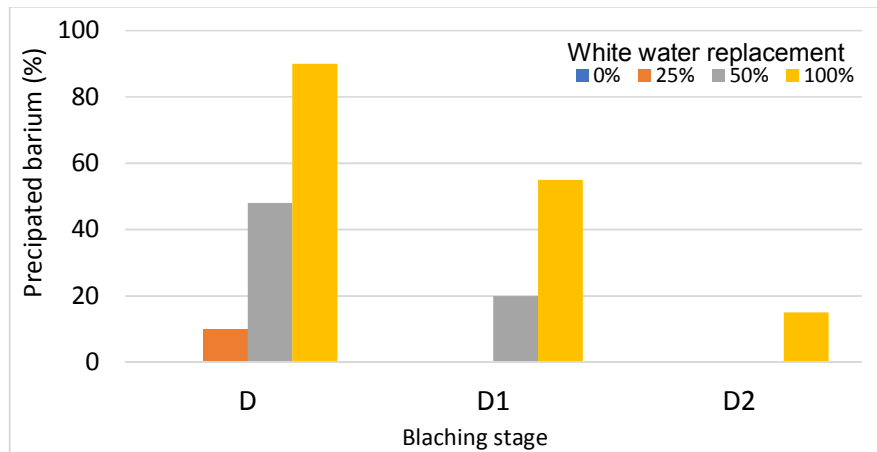


Figure 3 – Barite formation in acidic bleaching stages with white water replacement.

The barium concentration in the UF permeate was 5.7 times greater than in the whitewater and led to formation of scale deposits after 25% of whitewater where replaced (Figure 3). At this rate, the amount of barium in solid state (as barite) is 10%. All the calculations were carried out without considering the interaction of the barium and sulfate with the fiber. In some conditions, the barium can be adsorbed by the fibers (LITVAY et al., 2003). It is expected that with 25% of replacement the amount of barite formation will not be a critical problem. With 25% of replacement of whitewater it is possible to reduce the water consumption in 3.560 m<sup>3</sup>/d. The non-used whitewater can replace hot water in the (EPO) washer, and hot water reused within the mill replacing the clean water intake. Further studies must be carried out to determinate the feasibility of this water circuit.

In order to increase the replacement of the whitewater and reduce the water consumption it is necessary to reduce the amount of barium and sulfate in the fiberline. This can be achieved by improving the de-barking of the wood since the barium content of the bark it is much higher than in the stem wood (PERSSON

et al., 2002), and by changing the sulfuric acid as a pH regulator and control the carry-over from brownstock (RUDIE & HART, 2006).

With 50% of replacement of whitewater by the UF permeate, 50% of the barium formed barite and the risk of scaling increased considerably, considering that without permeate reuse the amount of barite is 0% (according to software simulation).

### Effects on the ETP

The characteristics of the treated effluent of the industrial ETP (average of 90 samples) and the results of the model simulation are presented in Table 6. The model was developed to obtain a steady-state condition and the results of Scenario 1 were used for validation of the model. The COD fractions obtained are presented in Table 5.

Table 5 – Biological model specifications

Parameter	Value
Readily biodegradable COD (gCOD/g of total COD)	0.45
Non-colloidal slowly biodegradable COD (gCOD/f of slowly degradable COD)	0.17
Unbiodegradable soluble COD (gCOD/g of total COD)	0.33
Unbiodegradable particulate COD (gCOD/g of total COD)	0.04

The simulated biological treatment had the same hydraulic retention time (14.5 h) and solid retention time (15 d). The VSS of the industrial biological reactor is 2.888 mg/L (mean of 90 samples) and the value obtained at Scenario 1 (reference) was 2.892 mg/L. The COD removal, NTK, and phosphorus for this scenario was statistically equal to the real values. There was a difference between the sludge production of 5.4% (larger), because this parameter depends of kinetic variables (GERNAEY et al., 2004), which some were assumed by the software (endogenous fraction, aerobic decay rate, maximum specific growth rate, etc.).

The results showed that in Scenario 2 (the ETP treats the UF-permeate) there was a reduction in the COD load of the final effluent by 38% and the waste biosludge production by 36% because of the decrease of the COD load of the affluent.

It is expected that in the actual biological treatment, the COD removal increase because the large organic molecules are retained by the membrane and the permeate had small size molecules that are biodegradable, i.e., there is an increase in the biodegradable organic matter ratio of the effluent. (MOUNTEER et al., 2007).

Table 6 – Effects of the UF on the treatment plant

<b>Parameter</b>	<b>Industrial</b>	<b>Scenario</b>			
	<b>ETP</b>	<b>1</b>	<b>2</b>	<b>3</b>	<b>4</b>
COD (mg/L)	241 ± 17	242	149	103	140
COD removal (%)	66 ± 2	67	67	67	67
Waste bioludge production (kg/d)	9211 ± 151	9713	6192	3348	5790
NTK (mg/L)	0.77 ± 0.2	1.20	1.13	1.1	1.18
Phosphorus (mg/L)	0.10 ± 0.01	0.2	0.17	0.2	0.17
TSS (mg/L)	6.01 ± 1.2	5.87	5.41	5.10	5.40

± Standard derivation. Scenario 1: simulate the biological treatment of the current industrial effluent as a reference; Scenario 2: simulate the biological effluent treatment without the acidic filtrate but with the added UF permeate; Scenario 3: simulate the biological effluent treatment without the acidic filtrate and without the UF permeate (the permeate from the UF was recycled within the mill) and Scenario 4: Simulate the biological treatment without the acidic filtrate; and with 25% of replacement of white water on the bleaching plant

If barium and sulfate is removed from the fiberline, it would be possible to implement Scenario 3 (100% of replace of whitewater). In this case it will decrease the water consumption in 25% and the operation cost related to aeration in 50%.

## CONCLUSIONS

The main conclusions of this works are as follow:

- i) It was possible to treat the acidic filtrate from a kraft pulp mill with ultrafiltration membranes, COD and color removal was 65% and 82% respectively.
- ii) The ultrafiltration treatment removed a fraction of metals and inorganics compounds from the acidic effluent without a pretreatment or pH adjustment.

- iii) Computer model simulation predicted that 25% of replacement generate a precipitation of 10% of the total barium and will reduce the COD and waste sludge production in 42% and 40%, respectively.
- iv) If all the permeate it is sent directly to the ETP, the COD of the final effluent and the waste biosludge production will reduce 38% and 36%, respectively.
- v) Further studies must be carried to determined the best usage of the retentate, the effects on the final product and on the chemical consumption in the bleaching plant.

## ACKNOWLEDGMENTS

We would like to thank the Universidade Federal de Viçosa, the Fundação de Amparo á Pesquisa do Estado de Minas Gerais (FAPEMIG) for the financial support and the Estudantes-Convênio de Pós-Graduação Program – PEC-PG, of CAPES/CNPq - Brazil

## REFERENCES

BAJPAI, P. Biological Treatment of Pulp and Paper Mill Effluents. In: **Biotechnology for Pulp and Paper Processing**. Boston, MA: Springer US, 2012. p. 211–261.

BERNAT, X.; SÁNCHEZ, I.; STÜBER, F.; BENGGOA, C.; FORTUNY, A.; FABREGAT, A.; FONT, J. Removal of heavy metals by ultrafiltration. In: European Congress of Chemical Engineering, September, Copenhagen. **Anais...** Copenhagen: ECCE-6, 2007.

BERNATA, X.; FORTUNY, A.; STÜBER, F.; BENGGOA, C.; FABREGAT, A.; FONT, J. Recovery of iron (III) from aqueous streams by ultrafiltration. **Desalination**, v. 221, n. 1–3, p. 413–418, 2008.

BRIAN N. BROGDON. Caustic Extraction in Elemental Chlorine-Free Bleaching Sequences for Softwood Kraft Pulps: A Fundamental Review and Analysis. In: TAPPI Engineering, Pulping & Environmental Conference, Portland. **Anais...** Portland: 2008.



COX, S. Nanofiltration as Pretreatment to Reverse Osmosis for Paper and Pulp Mill Effluent. In: IWA Regional Conference Membrane Technologies in Water and Waste Water Treatment, Moscow. **Anais...** Moscow: SIBICO International Ltd, 2006.

CULBERTSON, C.; TREASURE, T.; VENDITTI, R.; JAMEEL, H.; GONZALEZ, R. Life Cycle Assessment of lignin extraction in a softwood kraft pulp mill. **Nordic Pulp and Paper Research Journal**, v. 31, n. 1, p. 30–40, 2016.

DENCE, C.; REEVE, D. W. Pulp Bleaching. Atlanta: **TAPPI Press**, 1996.

DIONÍSIO, K.; CARDOSO, M.; NICOLATO, R. Process simulation for water consumption minimization in pulp mill. **Latin American Applied Research**, v. 40, n. 1, p. 81–90, 2010.

GERNAEY, K. V; VAN LOOSDRECHT, M. C. .; HENZE, M.; LIND, M.; JØRGENSEN, S. B. Activated sludge wastewater treatment plant modelling and simulation: state of the art. **Environmental Modelling & Software**, v. 19, n. 9, p. 763–783, 2004.

HUBER, P.; BURNET, A. A.; PETIT-CONIL, M. Scale deposits in kraft pulp bleach plants with reduced water consumption: a review. **Journal of environmental management**, v. 141, p. 36–50, 2014.

KASHER, R. Membrane-based water treatment technologies: Recent achievements, and new challenges for a chemist. **Bulletin of the Israel Chemical Society**, n. 24, p. 10–18, 2009.

LITVAY, C.; RUDIE, A.; HART, P. Use of Excel Ion Exchange Equilibrium Solver with WinGEMS to Model and Predict NPE Distribution in the MeadWestvaco Evandale, TX Hardwood Bleach Plant. In: Proceeding of the 2003 TAPPI Fall Technical Conference, Chicago. **Anais...** Chicago: TAPPI Press, 2003.

LUO, J.; WAN, Y. Effects of pH and salt on nanofiltration-a critical review. **Journal of Membrane Science**, v. 438, p. 18–28, 2013.

MOUNTEER, A. H.; SOUZA, L. C.; SILVA, C. M. Potential for Enhancement of Aerobic Biological Removal of Recalcitrant Organic Matter in Bleached Pulp Mill Effluents. **Environmental Technology**, v. 28, n. 2, p. 157–164, 2007.

NILSSON, M.; TRÄGÅRDH, G.; ÖSTERGREN, K. The influence of pH, salt and temperature on nanofiltration performance. **Journal of Membrane Science**, v. 312, n. 1, p. 97–106, 2008.

NORDIN, A. K.; JÖNSSON, A. S. Case study of an ultrafiltration plant treating bleach plant effluent from a pulp and paper mill. **Desalination**, v. 201, n. 1–3, p. 277–289, 2006.

OLSSON, M. R. Simulations of Evaporation Plants in Kraft Pulp Mills Including Lignin Extraction and Use of Excess Heat. **Chemical Engineering & Technology**, v. 24, p. 195-200, 2009.

PERSSON, M.; ULMGREN, P.; PULP, S. Deposition of barium sulfate in bleach plants . Part 1 : Solubility and factors affecting the precipitation in D ( chlorine dioxide )-filtrates. **Nordic Pulp And Paper Research Journal**, v. 17, n. 3, p. 280–287, 2002.

QIU, Y.-R.; MAO, L.-J. Removal of heavy metal ions from aqueous solution by ultrafiltration assisted with copolymer of maleic acid and acrylic acid. **Desalination**, v. 329, p. 78–85, 2013.

QUEZADA, R.; SILVA, C. M.; PASSOS REZENDE, A. A.; NILSSON, L.; MANFREDI, M. Membrane treatment of the bleaching plant (EPO) filtrate of a kraft pulp mill. **Water Science and Technology**, v. 70, n. 5, p. 843–50, 2014.

RUDIE, A.; HART, P. Modeling and minimization of barium sulfate scale. (TAPPI Press, Ed.) In: Engineering, Pulping & Environmental Conference, Atlanta. **Anais...** Atlanta: 2006.

SAIF, Y.; ALMANSOORI, A.; ELKAMEL, A. Wastewater minimization in pulp and paper industries through energy-efficient reverse-osmosis membrane processes. **Chemical Engineering and Technology**, v. 36, n. 3, p. 419–425, 2013.

SHARMA, R. R. E S. CHELLAM. Temperature Effects on the Morphology of Porous Thin Film Composite Nanofiltration Membranes. **Environmental Science & Technology**, v.39, n.13, 2005/07/01, p.5022-5030. 2005.

STOVER, R. Evaluation of closed circuit reverse osmosis for water reuse. In: Proc. 27th Annual Water Reuse Symp, Hollywood, FL. **Anais...** Hollywood, FL: Water Reuse Association, 2012.

VAN TRAN, A. Decreasing effluent loads through bleaching modification. **Water Research**, v. 40, n. 3, p. 487–494, 2006.

### **CAPITULO 3: TREATMENT OF BLEACHING PLANT EFFLUENT FROM A KRAFT PULP MILL BY ELECTROCOAGULATION PROCESS**

#### **ABSTRACT**

Acidic and alkaline effluent from a kraft pulp bleaching plant mill was treated by electrocoagulation (EC) process using aluminum and iron electrodes. The best COD removal was achieved in both cases (acidic and alkaline effluent) with aluminum electrodes. The COD and color removal of the acidic effluent was 51 and 90% respectively, and the COD and color removal of the alkaline effluent was 48 and 73%, respectively. The feasibility of the treated effluent reuse was evaluated by computer simulation using WinGEMS software and chemical speciation methods. According to the steady-state simulation, 100% of the hot water can be replaced with treated acidic or alkaline effluent without scaling of calcium carbonate. The effect of the EC treatment on the mill effluent treatment plant was evaluated using BioWin software simulation. Compared with the actual mill, the reuse of the treated acid effluent decreased the COD load in the final effluent by 57 %, the waste biosludge generation by 30% and water consumption by 21%.

*Keywords: Electrocoagulation, bleaching effluent, simulation process, water reuse.*

#### **INTRODUCTION**

The pulp and paper mills consume large amounts of fresh water and therefore discharge proportionally large volume of effluents. Pulp mills worldwide have been required to develop ways to minimize water consumption and effluent discharges.

The treatment of specific in-plant streams seems to be an attractive technical and economical approach because it allows the use of advance technologies such as membrane filtration (QUEZADA et al., 2014) and electrocoagulation (ZAIED & BELLAKHAL, 2009).

Traditional methods for dealing with the wastewater consist of biological, physical, and chemical processes and their different combinations. The typical treatment processes for pulp and paper effluents are chemical precipitation, aerated lagoons and activated sludge.

Physical chemical technologies such as coagulation/flocculation by chemical precipitation include three stages of solid/liquid removal. First, the chemical agent is added to the water to destabilization of the pollutants; second, the formation of larger particles via slow mixing, which promotes the collision of the particles and the consequent aggregation; and third step is the solid-liquid separation by sedimentation or flotation of the formed flocs. In the conventional treatment chemicals such as polymers, iron and aluminum salts are used (HOLT et al., 2005).

Despite the availability of the above mentioned methods, effluent treatment alternatives with comparative advantages, such as automation of processes and cost, have been studied, highlighting the electrocoagulation (EC) as a promising technology (CHEN, 2004).

In electrocoagulation process, an electrochemical reactor carries out the steps of convectional coagulation providing the coagulant “in situ”. It is based on dissolution of the electrode material used as an anode. This so-called “sacrificial anode” produces metal ions which act as coagulant agents in the aqueous solution. The electrodes are usually made of aluminum, iron, or stainless steel (EMAMJOMEH & SIVAKUMAR, 2009).

During EC, the following main reactions with the metal (M) take place at the electrodes:

Anode:



Cathode:



Electrochemically generated metal cations will react spontaneously, forming various monomeric species, in the case of aluminum anode, such as  $Al(OH)_2^{+}$ ,  $Al_2(OH)_2^{4+}$ , and  $Al(OH)_4^{-}$  and polymeric species such as  $Al_6(OH)_{15}^{3+}$ ,  $Al_7(OH)_{17}^{4+}$ ,  $Al_8(OH)_{20}^{4+}$ ,  $Al_{13}O_4(OH)_{24}^{4+}$  and  $Al_{13}(OH)_{34}^{5+}$ .

Advantages of EC over conventional coagulation process include economic aspects (relatively low investment cost, maintenance, energy, and treatment costs), significantly lower volume of sludge produced, better sludge quality (lower water content, larger and more stable flocs with better settlability), similar or slightly better efficiency, avoidance of chemical addition, ease of automation, simple and compact size of EC system, broad functional pH range and pH neutralization effect, and the presence of electroflotation (MOLLAH et al., 2001). However, limited researches have been reported the treatment of pulp bleaching effluent using EC method (SRIDHAR et al., 2011).

After EC treatment, a clean water is generated. To develop a water conservation program in a mill, it is necessary to reuse this stream without risking the mill process. The accumulation of elements and compounds in the water cycle can cause severe problems in the mill (PARTHASARATHY & KRISHNAGOPALAN, 2001; DOLDÁN et al., 2011); the most common in the bleach plant is the formation of barium sulfate, calcium carbonate and calcium oxalate (DUGGIRALA, 2005; HUBER et al., 2014).

Scaling occurs when part of the dissolved solids in a solution precipitates, which leads to the formation of layer of solids over contacting surfaces. Scaling is, therefore, intimately related to the solubility of the compounds present in solution (ANTONY et al., 2011). In order to predict the relative solubility of some compounds, it is possible to simulate these phenomena using computer simulation software (AMIRI & MOGHADASI, 2010).

The objectives of this study were to i) evaluate the influence of current density, initial pH, electrode material and process time on the electrocoagulation treatment of bleaching plant effluents, ii) develop a software simulation tool to evaluate the feasibility of recycling the clean treated effluents in the bleach plant and iii) determinate the effects on the effluent treatment plant.

## **MATERIAL AND METHODS**

### **Effluent**

The characteristics of the acidic and the alkaline effluents from the bleaching plant (Figure 1) of a softwood kraft pulp mill were measured. The COD, color, conductivity and metals (3 samples) were determined according to Standard Methods for the Examination of Water (APHA, 2005). The acidic

effluent was obtained from the wash press of the  $D_0$  stage and the alkaline effluent from the wash press from the EOP stage, during normal operation of the mill. All samples were stored at 5°C.

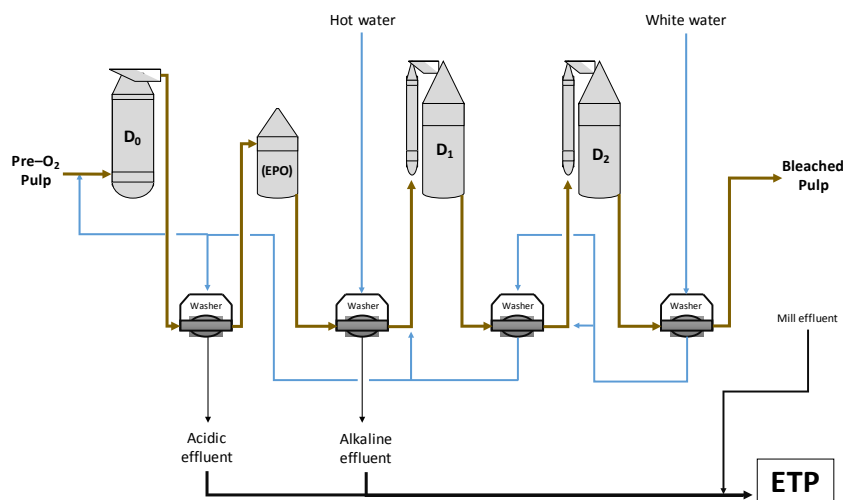


Figure 1 – Bleaching process and the generated effluents

## Electrocoagulation

The electrocoagulation (EC) test was carried in a 2L batch electrochemical reactor (Figure 2) with 8 plates (electrodes) of 13 x 15 cm each and a distance between the electrodes of 1.4 cm approximately. The connection with the power source was in parallel, this way the electrodes are monopolar. The EC treatment was carried out under constant stirring of 150 rpm. The design of the electrochemical reactor was based from prevews studies (VALENTE et al., 2012). The initial temperature of the effluent was approximately 25 °C.

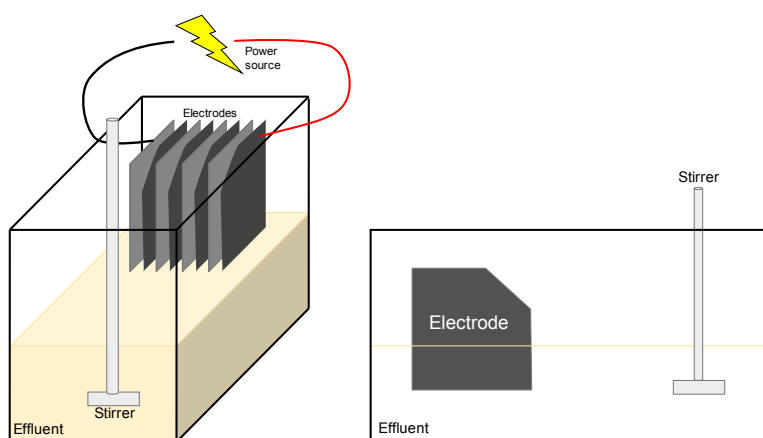


Figure 2 – Electrochemical reactor.

Two different types of materials for the construction of the electrodes were tested, aluminum (99% pure) and iron (99.45% pure). For each type of electrode, it was evaluated the influence of the initial pH, current density (amount of electric flowing per unit cross-sectional area of material) and the time of reaction.

For each effluent (acidic and alkaline) was evaluated the electrocoagulation with both electrodes composition (aluminum and iron) (Table 1). The experimental design was a Box-Behnken type. It was made 12 combinations among the levels of the three factors (pH, current density and time) and five replicates related to the combination center point for estimation of the residual error, totaling 17 experiments per electrode/effluent (68 tests considering both electrodes material and both effluents). The conditions were selected according to previous research (CHANWORRAWOOT & HUNSOM, 2012).

The pH of the sample was adjusted to the condition of the experimental design using NaOH or H<sub>2</sub>SO<sub>4</sub>. After the treatment, separation of liquid and solid was carried out by sedimentation for a period of 30 minutes. The COD, color and metals were determined by according to Standard Methods for the Examination of Water (APHA, 2005).

Table 1 – Experimental variables

Variable	Acidic Effluent		Alkaline Effluent	
	Min	Max	Min	Max
pH	3	7	7	12.6
Current intensity (A)	3.12	9.36	3.12	9.36
Reaction time (min)	10	60	10	60

### Process simulation

The feasibility of the reuse of the effluent treated with EC was studied by process simulation, to determined the potential of scaling formation of barium sulfate (in the acidic stage), calcium carbonate and magnesium hydroxide (in the alkaline stage).

For mill simulations it was used about 30 data sets, containing about 5 variables per set collected at the mill and a full characterization of metals, salts, organic matter was made.



Data and the information entry to the WinGEMS models involve solving mass and energy process balances through interactive calculations. Given the complexity of the bleach plant and the non-process elements (NPE) distribution, it was necessary to develop a new block with the Pitzer electrolytic solutions model for calculation of chemical equilibrium. The Pitzer model uses as input data the composition of a given solution (in terms of molality, or moles of component per kg of solvent), as well as the several thermodynamic parameters.

Using the simulation model, the hot water added to the (EPO) press-washer was replaced by the acidic or alkaline treated effluent. The simulations were run, in each case, to the steady-state condition at water replacement rates of 0, 25, 50, 75 and 100%.

### **Effects on the Effluent Treatment Plant (ETP)**

The effects of the treatment with electrocoagulation of the acidic effluent and/or the alkaline effluent, on the effluent treatment plant (ETP) were evaluated by process simulation in BioWin™ (EnviroSim) software. It was determined the final effluent characteristics and sludge production. The mill's effluent biological treatment plant consists of an activated sludge (extended aeration) plant. Each line is constituted by 4 biological aerated selectors (2.1, 1.7, 0.9 and 0.9 h of retention time), a bioreactor (8.9 h of retention time) and a secondary clarifier.

Five scenarios were evaluated for hot water replacement. Scenario 1: simulate the biological treatment of the existing industrial effluent plant as reference; Scenario 2: simulate the biological effluent treatment without the acidic effluent but with the added acidic treated effluent (EC with aluminum electrode treatment); Scenario 3: simulate the biological effluent treatment without the acidic effluent and without treated acid effluent (the treated effluent from the EC was recycled within the mill); Scenario 4: simulate the biological effluent treatment without the alkaline effluent but with the added treated alkaline effluent (EC with aluminum electrode treatment), and Scenario 5: simulate the biological effluent treatment without the alkaline effluent and without treated alkaline effluent (the treated effluent from the EC was recycled within the mill).

## RESULTS AND DISCUSSION

### Effluent characterization

The characterization of the acidic and alkaline effluent samples is presented in Table 2.

Table 2 – Acidic and alkaline effluent characterization

Parameter (mg/L)	Acidic effluent	Alkaline effluent
COD	1650 ± 31	1035 ± 20
Color	755 ± 16	810 ± 7
Na	170 ± 13	184 ± 8
Ca	14.1 ± 1.3	4.7 ± 0.7
K	15.3 ± 1.8	6.9 ± 0.6
Mg	1.68 ± 0.12	0.29 ± 0.03
Mn	0.31 ± 0.03	0.03 ± 0.01
Ba	0.06 ± 0.01	0.04 ± 0.01
Al	0.49 ± 0.03	0.16 ± 0.01
Cu	0.03 ± 0.01	0.04 ± 0.01
Si	0.54 ± 0.01	0.57 ± 0.01
P	1.16 ± 0.03	0.39 ± 0.01
Fe	0.36 ± 0.01	0.17 ± 0.01
SO <sub>4</sub>	910 ± 50	250 ± 12

\*Average of three samples

### Electrocoagulation of acidic effluent

The results of the electrocoagulation treatment of the acidic effluent with aluminum electrodes is presented in the Figure 3. According to the statistical analysis, the optimum point for the COD removal was obtained for the initial pH 3.4, the current density 120 A/m<sup>2</sup> and the reaction time of 50 minutes. At this condition, the final pH was 8 and the COD and color removal was 51% and 90%, respectively, considering the reactor volume and the electrode area, the removal of COD and color was 8 g/Lm<sup>2</sup> and 12.000 CU/Lm<sup>2</sup>, respectively.

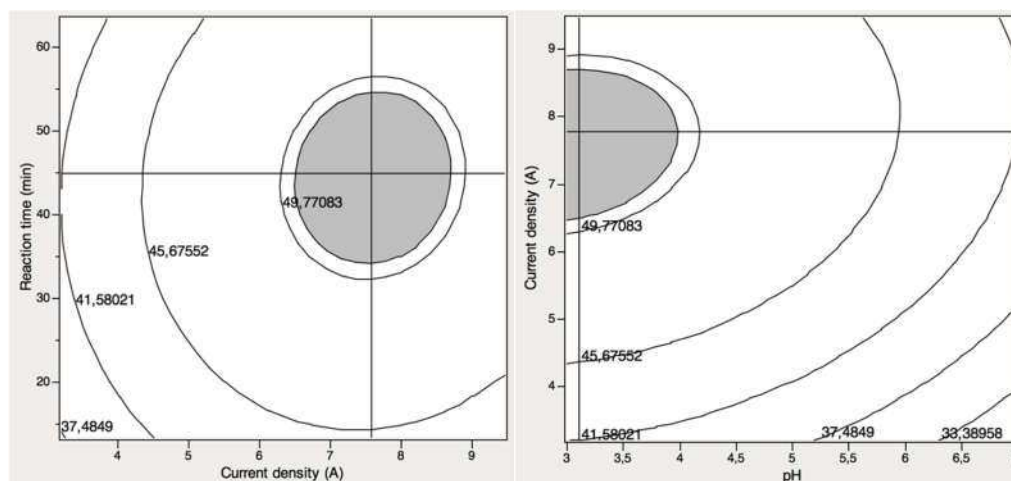


Figure 3 – Contour profiler of the COD removal with electrocoagulation using aluminum electrode.

The obtained flocs were well formed, stable and compacted, they floated with the  $H_2$  generated in the reaction. This flotation phenomenon was described by other authors as advantages of the electrocoagulation process (MOLLAH et al., 2001; BUTLER et al., 2011; KHANDEGAR & SAROHA, 2013; SAHU et al., 2014). At the optimum COD removal conditions, the sludge production was 0.21 g per liter of effluent treated, i.e., the treatment of all the acidic effluent will generate 2.7 t/d of sludge. Further studies must be carried out to determined the best sludge treatment/disposal strategy.

Other advantage of this process is the metals removal, which was observed in this study and reported by other authors (EMAMJOMEH & SIVAKUMAR, 2009; KABDAŞLI et al., 2009; CHATURVEDI, 2013; PULKKA et al., 2014). The reduction of the heavy metals is presented in Table 3. The treated effluent had an increase of 1700% in the aluminum concentration after the treatment.

Table 3 – Elements removal of the acidic effluent using electrocoagulation with aluminum electrode

Element	Na	Ca	K	Mg	Mn	Ba	Al	Cu	Si	P	Fe
Removal (%)	0	60	3	65	86	31	-1700	0	100	72	31

The results of the electrocoagulation treatment of the acidic effluent with iron electrode is presented in the Figure 4.

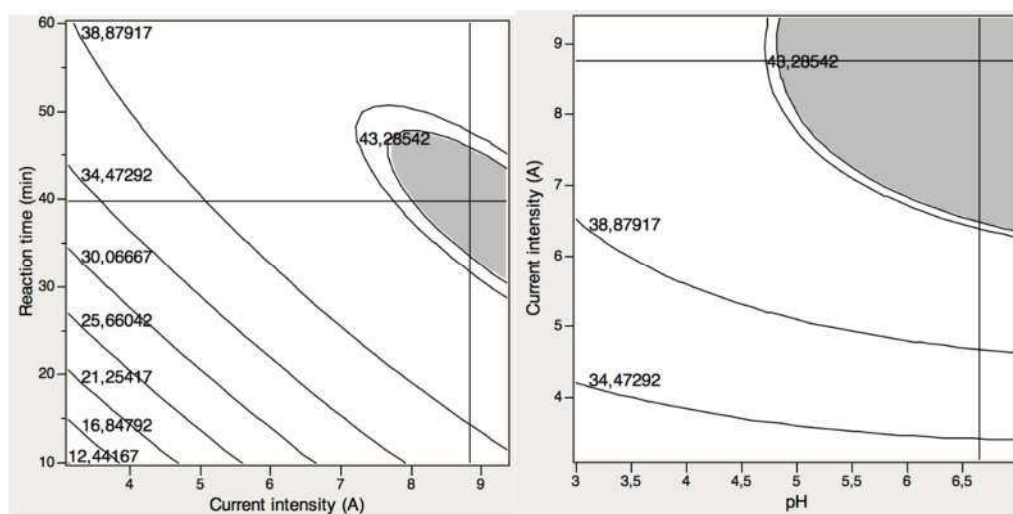


Figure 4 - Contour profiler of the COD removal with electrocoagulation using iron electrode.

The obtained flocs were well formed and most of them floated with the  $H_2$  generated in the reaction. According to the statistical analysis the optimum point for the COD removal was obtained when the initial pH was 7, the current density  $144 \text{ A/m}^2$  and the reaction time 50 minutes. At this condition, the final pH was 11 and the COD and color removal was 47% and 66%, respectively. Considering the reactor volume and the electrode area, the removal of COD and color was  $7,8 \text{ g/Lm}^2$  and  $11.700 \text{ CU/Lm}^2$ . The color removal was lower than the treatment with aluminum electrode because of the orange coloring of the effluent due to the presence of  $Fe(OH)$  (MOLLAH et al., 2001; MORENO et al., 2007; CHATURVEDI, 2013). In order to have COD and color removal larger than 20% the pH of the effluent, it must be increased to at least 5. This pH adjustment affects directly on the treatment cost. The reduction of the elements is presented in the Table 4.

Table 4 – Elements removal of the acid effluent using electrocoagulation with iron electrode

Element	Na	Ca	K	Mg	Mn	Ba	Al	Cu	Si	P	Fe
Removal (%)	0	77	0	80	100	67	80	0	100	88	-297

For the treatment of the acidic effluent, the EC with aluminum electrode achieved the higher COD and color reduction without pH adjustment, i.e, more

suitable treatment to generate an effluent capable to be reused within the process.

If the treated effluent is reused within the acidic or alkaline stage, pH, COD, calcium, hydroxide and barium amount are critical parameters, because of the risk of scaling formation (HUBER et al, 2014) and the increase of chemical dosage for bleaching (COLODETTE et al., 2006; JANNE et al., 2013; KOSSAR, 2013). Because of pH and elemental composition, the treated acidic effluent was evaluated to be reused within the process, replacing hot water in the EPO-washer.

### Electrocoagulation of alkaline effluent

The results of the analysis of the electrocoagulation treatment of the alkaline effluent with aluminum electrode is presented in the Figure 5.

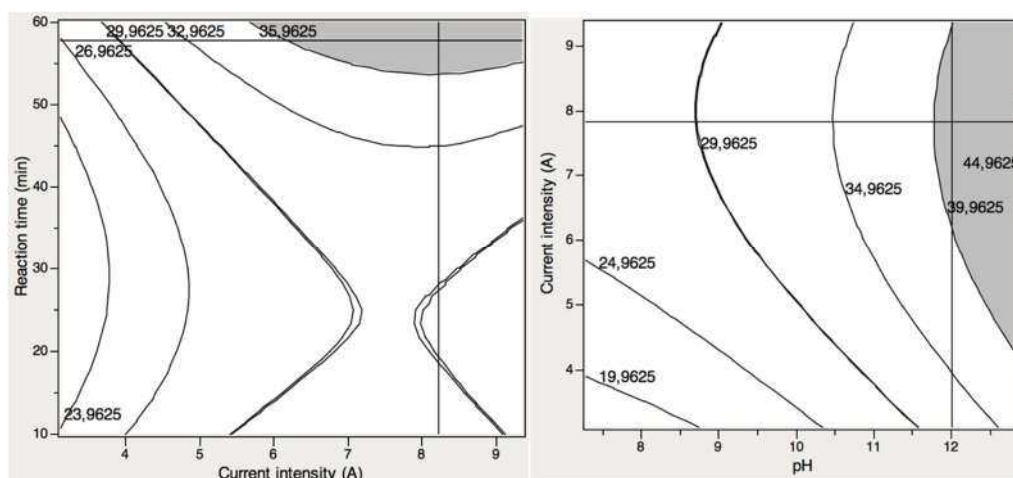


Figure 5 - Contour profiler of the COD removal with electrocoagulation using aluminum electrode

According to the statistical analysis the optimum point for the COD removal was obtained when the initial pH is 11, the current density  $120 \text{ A/m}^2$  and the reaction time 50 minutes. At this condition, the COD and color removal was 48% and 73%, respectively. Considering the reactor volume and the electrode area, the removal of COD and color was  $7.2 \text{ g/Lm}^2$  and  $8.800 \text{ CU/Lm}^2$ . The obtained flocs were well formed, stables compacted and uncolored, they floated with the  $\text{H}_2$  generated in the reaction. The sludge production was 2.1 t/d of sludge.

The reduction of the elements is presented in the Table 5. The amount of aluminum increased in the effluent as described by other authors (BOROSKI et al., 2008; TERRAZAS et al., 2010; BUTLER et al., 2011; SAHU et al., 2014) because of the dissolution of the electrode.

Table 5 – Elements removal of the alkaline effluent using electrocoagulation with aluminum electrode

Element	Na	Ca	K	Mg	Mn	Ba	Al	Cu	Si	P	Fe
Removal (%)	0	82	49	90	100	67	-1951	0	100	90	0

The results of the analysis of the electrocoagulation treatment of the alkaline effluent with iron electrode is presented in the Figure 6.

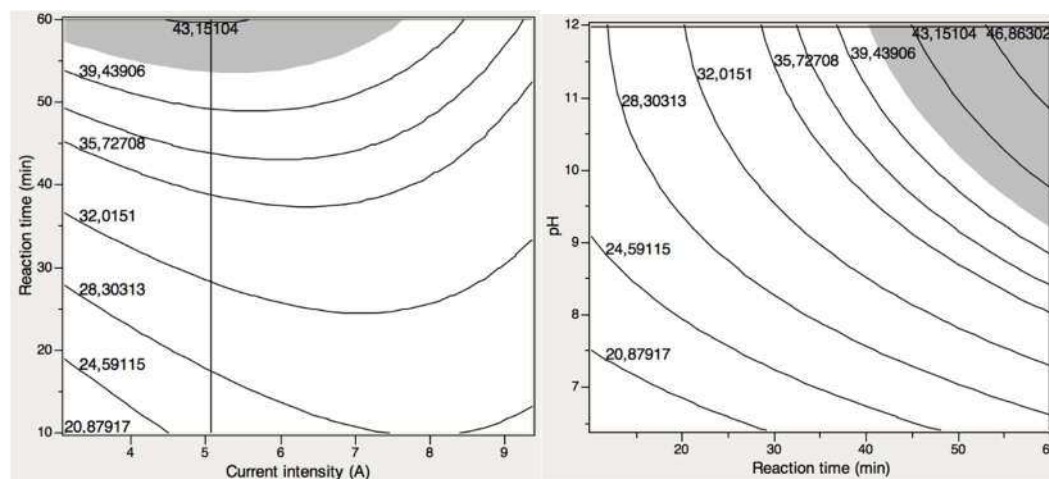


Figure 6 - Contour profiler of the COD removal with electrocoagulation using iron electrode

According to the statistical analysis, the optimum point for the COD removal was obtained when the initial pH was 10, the current density 85 A/m<sup>2</sup> and the reaction time 50 minutes. At this condition, the COD and color removal was 43% and 51%, respectively. Considering the reactor volume and the electrode area, the removal of COD and color was 7.5 g/Lm<sup>2</sup> and 6.800 CU/Lm<sup>2</sup>.

The reduction of the heavy metals is presented in Table 6. The color removal was lower than the treatment with aluminum electrode because of the orange coloring of the effluent due to the presence of Fe(OH).

Table 6 – Elements removal of the alkaline effluent using electrocoagulation with iron electrode

Element	Na	Ca	K	Mg	Mn	Ba	Al	Cu	Si	P	Fe
Removal (%)	0	57	33	60	100	55	87	0	100	79	-111

For the treatment of the alkaline effluent the electrocoagulation with aluminum electrode achieved a higher COD and color reduction. Because of elemental composition, the treated alkaline effluent was evaluated to be reused within the process replacing hot water in the EPO-washer.

### Process simulation and clean water reuse

The calcium carbonate formation in the (EPO) filtrate can be a critical parameter causing operational problems in the bleach plant because of scaling, particularly on the pulp washers. In the treated acidic effluent (with EC using aluminum electrode), the calcium concentration was higher (5.6 mg/L) than in the hot water (1.6 mg/L) and, therefore, it increased when the treated effluent reuse increased. Also, a higher concentration of carbonate ions in the treated effluent (410 mg/L) compared to hot water (were it could not be detected) increased the formation of calcium carbonate in the (EPO) filtrate (Figure 7).

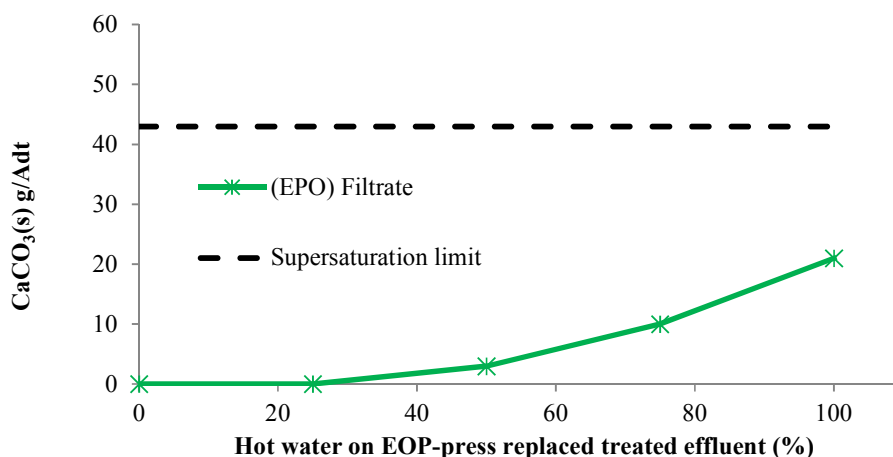


Figure 7 - Calcium carbonate formation in the (EPO) filtrate with hot water replacement with treated acidic effluent

In the treated alkaline effluent (EC with aluminum electrode), the calcium concentration was lower (0.8 mg/L) than in the treated acidic effluent (5.6 mg/L) and in the hot water (1.6 mg/L), therefore, the Ca concentration decreased when the treated effluent reuse increased. Also, the concentration of carbonate ions in

the treated effluent (75 mg/L) was lower compared to the treated acidic effluent. With 100% of replacement, software simulation indicated that there is not calcium carbonate in the (EPO) filtrate.

In both cases (acidic treated effluent or alkaline treated effluent reuse), simulation predicts that 100% replacement of hot water in the EOP press should be technically possible (saving 7.5 m<sup>3</sup>/ADt). Supersaturation calculations indicate that the precipitation of calcium carbonate will not start even with 100% of the hot water being replaced.

### Effects on the Effluent Treatment Plant (ETP)

The characteristics of the treated effluent of the industrial ETP and the results of the model simulation with treatment of the acidic effluent (EC with aluminum electrode) are presented in Table 8, and the results with treatment of the alkaline effluent (EC with aluminum electrode) are presented in Table 9.

Table 8 - Effects of the EC treatment of the acidic effluent on the treatment plant

Parameter	Industrial	Scenarios		
	ETP	1	2	3
COD (mg/L)	241 ± 17	242	165	103
COD removal (%)	66 ± 2	67	67	67
Waste Sludge production (kg/d)	9211 ± 151	9713	6912	6192
NTK (mg/L)	0.77 ± 0.2	1.20	1.17	1.13
Phosphorus (mg/L)	0.10 ± 0.01	0.2	0.15	0.17
TSS (mg/L)	6.01 ± 1.2	5.87	5.7	5.41

± Standard derivation

In the scenarios where the effluent from EC is sent to the effluent treatment plant (Scenarios 2 and 4) it is expected that there will have a reduction in the COD of the final effluent and in the waste sludge production because of the decrease of the COD load of the effluent.



Table 9 - Effects of the EC treatment of the alkaline effluent on the treatment plant

Parameter	Industrial ETP	Scenarios	
		4	5
COD (mg/L)	241 ± 17	186	121
COD removal (%)	66 ± 2	67	67
Waste Sludge production (kg/d)	9211 ± 151	7421	6410
NTK (mg/L)	0.77 ± 0.2	1.3	1.2
Phosphorus (mg/L)	0.10 ± 0.01	0.15	0.16
TSS (mg/L)	6.01 ± 1.2	5.5	5.5

± Standard derivation

In Scenario 3 (EC treatment of the acidic effluent and reuse replacing hot water), the COD of the final effluent and the waste sludge production decreased in 57% and 36%, respectively, when compared to the reference. In the Scenario 5 (EC treatment of the alkaline effluent and reuse replacing hot water) the COD of the final effluent and the waste sludge production decreased in 50% and 33%, respectively, when compared to the reference. In both cases (Scenario 3 and 5) the water economy was 7.4 m<sup>3</sup>/ADt.

## CONCLUSIONS

The main conclusions of this work are:

- i) The best removal of COD and color of the acid effluent was achieved with electrocoagulation treatment with aluminum electrode, with a removal of COD and color was 8 g/Lm<sup>2</sup> and 12.000 CU/Lm<sup>2</sup>.
- ii) The best removal of COD and color of the alkaline effluent was achieved with electrocoagulation treatment with aluminum electrode, with a removal of COD and color was 8 g/Lm<sup>2</sup> and 8.800 CU/Lm<sup>2</sup>.
- iii) If treated acidic effluent is reused to replace 100% hot water in the (EPO)-press the amount of CaCO<sub>3</sub> will increase 20 g/ADt but will not achieve the supersaturating limit (no precipitation).
- iv) If treated alkaline effluent is reused to replace 100% of hot water in the EPO-press it is not expected to have scaling formation by CaCO<sub>3</sub> precipitation.
- v) The reuse of the treated acidic or alkaline effluent within the bleaching plant will improve the final effluent characteristics, the biowaste sludge generation and the water consumption.

- vi) Further studies must be carried to determine the best treatment/disposal strategy of the electrocoagulation sludge and the effects of the water reuse on the final product.
- vii) Further studies must be carried to determine the impact of the aluminum in the process and the product during treated effluent reuse.

## ACKNOWLEDGMENTS

We would like to thank the Universidade Federal de Viçosa, the Fundação de Amparo à Pesquisa do Estado de Minas Gerais (FAPEMIG) for the financial support and the Estudantes-Convênio de Pós-Graduação program – PEC-PG, of CAPES/CNPq - Brazil

## REFERENCES

AMIRI, M.; MOGHADASI, J. Prediction the Amount of Barium Sulfate Scale Formation in Siri Oilfield using OLI ScaleChem Software. **Asian Journal of Scientific Research**, v. 3, n. 4, p. 230–239, 2010.

ANTONY, A.; LOW, J. H.; GRAY, S.; CHILDRESS, A. E.; LE-CLECH, P.; LESLIE, G. Scale formation and control in high pressure membrane water treatment systems: A review. **Journal of Membrane Science**, v. 383, n. 1–2, p. 1–16, 2011.

BOROSKI, M.; RODRIGUES, A. C.; GARCIA, J. C.; GEROLA, A. P.; NOZAKI, J.; HIOKA, N. The effect of operational parameters on electrocoagulation-flotation process followed by photocatalysis applied to the decontamination of water effluents from cellulose and paper factories. **Journal of Hazardous Materials**, v. 160, p. 135–141, 2008.

BUTLER, E.; HUNG, Y.-T.; YEH, R. Y.-L.; SULEIMAN AL AHMAD, M. Electrocoagulation in Wastewater Treatment. **Water**, v. 3, n. 4, p. 495–525, 2011.

CHANWORRAWOOT, K.; HUNSOM, M. Treatment of wastewater from pulp and paper mill industry by electrochemical methods in membrane reactor. **Journal of Environmental Management**, v. 113, p. 399–406, 2012.

CHATURVEDI, S. I. Mercury Removal Using Fe–Fe Electrodes by Electrocoagulation. **International Journal of Modern Engineering Research**, v. 3, n. 1, p. 101–108, 2013.

CHEN, G. Electrochemical technologies in wastewater treatment. **Separation and Purification Technology**, v. 38, n. 1, p. 11–41, 2004.

COLODETTE, J. L.; GOMES, C. M.; RABELO, M. S.; EIRAS, K. M. M.; GOMES, A. F.; OLIVEIRA, K. D. Branqueamento de Polpa Kraft de Eucalipto: nível atual da técnica e novos desenvolvimentos. **O Papel**, v. 67, n. 9, p. 88-110, 2006

DOLDÁN, J.; POUKKA, O.; SALMENOJA, K.; BATTEGAZZORE, M.; FERNANDEZ, V.; ELUÉN, I. Evaluation of sources and routes of non-process elements in a modern eucalyptus kraft pulp mill. **O Papel**, v. 72, n. 7, p. 47–52, 2011.

DUGGIRALA, P. Formation of calcium carbonate scale and control strategies in continuous digesters. CD del II Coloquio Internacional sobre Celulosa ..., 2005.

EATON, A.D.; CLESCERI, L.S.; RICE, E.W.; GREENBERG, A.E.; Standard Methods for the Examination of Water & Wastewater. **Ed. 21, American Public Health Association USA (APHA)**, 2005.

EMAMJOMEH, M. M.; SIVAKUMAR, M. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes. **Journal of Environmental Management**, v. 90, n. 5, p. 1663–1679, 2009.

HOLT, P. K.; BARTON, G. W.; MITCHELL, C. A. The future for electrocoagulation as a localized water treatment technology. **Chemosphere**, v. 59, n. 3, p. 355–67, 2005.

HUBER, P.; BURNET, A. A.; PETIT-CONIL, M. Scale deposits in kraft pulp bleach plants with reduced water consumption: a review. **Journal of Environmental Management**, v. 141, p. 36–50, 2014.

JANNE, V.; RÅMARK, H.; TERVOLA, P. Reuse of purified effluent in the fiber line-laboratory results. **IPPTA: Quarterly Journal of Indian Pulp and Paper Technical Association**, v. 25, n. 1, p. 51–56, 2013.

KABDAŞLI, I.; ARSLAN, T.; ÖLMEZ-HANCI, T.; ARSLAN-ALATON, I.; TÜNAY, O. Complexing agent and heavy metal removals from metal plating effluent by electrocoagulation with stainless steel electrodes. **Journal of Hazardous Materials**, v. 165, p. 838–845, 2009.

KHANDEGAR, V.; SAROHA, A. K. Electrocoagulation for the treatment of textile industry effluent - A review. **Journal of Environmental Management**, v. 128, p. 949–963, 2013.

KOSSAR, M. J. Proposal for water reuse in the Kraft pulp and paper industry. **Water Practice & Technology**, v. 8, n. 3–4, p. 359–374, 2013.

MOLLAH, M. Y.; SCHENNACH, R.; PARGA, J. R.; COCKE, D. L. Electrocoagulation (EC)--science and applications. **Journal of hazardous materials**, v. 84, p. 29–41, 2001.

MORENO, H. A. C.; COCKE, D. L.; GOMES, J. A. G.; MORKOVSKY, P.; PARGA, J. R.; PETERSON, E.; GARCIA, C. Electrochemistry behind Electrocoagulation using Iron Electrodes. **ECS Transactions**, v. 6, n. 9, p. 1–15, 2007.

PARTHASARATHY, G.; KRISHNAGOPALAN, G. Systematic reallocation of aqueous resources using mass integration in a typical pulp mill. **Advances in Environmental Research**, v. 5, n. 1, p. 61–79, 2001.

PULKKA, S.; MARTIKAINEN, M.; BHATNAGAR, A.; SILLANPÄÄ, M. Electrochemical methods for the removal of anionic contaminants from water – A review. **Separation and Purification Technology**, v. 132, p. 252–271, 2014.

QUEZADA, R.; SILVA, C. M.; PASSOS REZENDE, A. A.; NILSSON, L.; MANFREDI, M. Membrane treatment of the bleaching plant (EPO) filtrate of a kraft pulp mill. **Water Science and Technology**, v. 70, n. 5, p. 843–50, 2014.

SAHU, O.; MAZUMDAR, B.; CHAUDHARI, P. K. Treatment of wastewater by electrocoagulation: A review. **Environmental Science and Pollution Research**, v. 21, n. 4, p. 2397–2413, 2014.

SRIDHAR, R.; SIVAKUMAR, V.; PRINCE IMMANUEL, V.; PRAKASH MARAN, J. Treatment of pulp and paper industry bleaching effluent by electrocoagulant process. **Journal of Hazardous Materials**, v. 186, n. 2–3, p. 1495–502, 2011.

TERRAZAS, E.; VÁZQUEZ, A.; BRIONES, R.; LÁZARO, I.; RODRÍGUEZ, I. EC treatment for reuse of tissue paper wastewater: aspects that affect energy consumption. **Journal of Hazardous Materials**, v. 181, n. 1–3, p. 809–16, 2010.

TONER, J. D.; CATLING, D. C.; LIGHT, B. A revised Pitzer model for low-temperature soluble salt assemblages at the Phoenix site, Mars. **Geochimica et Cosmochimica Acta**, v. 166, p. 327–343, 2015.

VALENTE, G. F. S.; SANTOS MENDONÇA, R. C.; PEREIRA, J. A. M.; FELIX, L. B. The efficiency of electrocoagulation in treating wastewater from a dairy industry, Part I: Iron electrodes. *Journal of environmental science and health. Part. B, Pesticides, Food Contaminants And Agricultural Wastes*, v. 47, n. 4, 2012.

WEBER, C. F. Calculation of Pitzer Parameters at High Ionic Strengths. **Industrial & Engineering Chemistry Research**, v. 39, n. 11, p. 4422–4426, 2000.

ZAIED, M.; BELLAKHAL, N. Electrocoagulation treatment of black liquor from paper industry. **Journal of Hazardous Materials**, v. 163, n. 2–3, p. 995–1000, 2009.

## CONCLUSÕES GERAIS

No capítulo 1, mediante simulação por software foi determinado que é possível o reúso do permeado de ultrafiltração do filtrado alcalino. Quando é substituída 100% da água quente na prensa EPO, aumenta o risco de formação de carbonato de cálcio, mas não atinge o nível de supersaturação (precipitação). Além, foi determinado que é possível dispor o concentrado da ultrafiltração no ciclo de recuperação química sem afetar o funcionamento da caldeira de recuperação.

No capítulo 2, foi determinado que o tratamento do filtrado ácido com membranas de ultrafiltração é possível e a remoção de DQO e cor foi 65% e 82%, respectivamente. O permeado pode substituir a água branca na prensa D0, mas com 25% de substituição aumenta em 10% o risco de formação de incrustações de sulfato de bário. Neste caso, o DQO do efluente final e a geração de lodo biológico na estação de tratamento de efluente diminui em 38 e 36% respectivamente.

No capítulo 3, a maior remoção de DQO, cor e metais dos filtrados ácido y alcalino foi obtida com o tratamento de eletrocoagulação com eletrodos de alumínio. Foi determinado com simulações em software que o 100% da água quente pode ser substituída com filtrado ácido ou alcalino tratado sem gerar a incrustação de carbonato de cálcio na prensa EOP. A substituição da água quente com alguma corrente interna da fábrica gera uma economia de água de 7.5 m<sup>3</sup>/ADt.

## ANEXO A

### SCALING MODEL IMPLEMENTATION

#### Inputs and outputs.

The Pitzer model takes as input the composition a given solution (in terms of molality, or moles of component per kg of solvent), as well as several thermodynamic parameters to be described. As output, it calculates the activity coefficient of each component in solution.

#### Activities

Electrolytic solutions are known to deviate considerably from what is known as an ideal solution. Under this idealization, the electrostatic interactions between the particles of solvent and those of solute - solvent-solute interactions - would be identical to solvent-solvent and solute-solute interactions. In order to account for such deviations, thermodynamics has introduced the concept of activity. Activity is sometimes thought as the effective concentrations that a compound in a solution. If the concentration (in molal) of a certain component  $C$  in solution is  $m_C$ , then its activity  $a_C$  is defined as:

$$a_C = \gamma_C m_C \quad \text{EQ 1}$$

where  $\gamma_C$  is known as the activity coefficient of  $C$ . This coefficient would equal unity if the solution were ideal, which is not usually the case.

#### Model parameters

The Pitzer model requires that several parameters be provided so that it may accurately describe the solutions under study. We may divide them into the following categories:

- a) **Electrolyte-specific parameters:** Parameters related to each specific electrolyte present in the system (e.g.  $\text{Na}_2\text{SO}_4$ ,  $\text{NaOH}$ , etc.). There are six such parameters, namely  $\alpha_1$ ,  $\alpha_2$ ,  $\beta_0$ ,  $\beta_1$ ,  $\beta_2$  and  $C^\phi$ .
- b) **Ion interaction parameters:** These parameters measure the effect of electrical interactions that occur between pairs and triplets of ions (binary and ternary interactions, respectively). The number of these

parameters grows with the number of types of ions in the system, as more combinations will be possible. The binary interaction parameters are often written as  $\theta_{ij}^*$ , whereas the ternary parameters are written as  $\Psi_{ijk}$ .

### Equilibrium data

In order to determine the solubility of a given electrolyte it is necessary to know the value of its solubility product,  $K_{sp}$ , under the conditions to which it is exposed. These data were obtained from the following sources: (Zemaitis, Clark, Rafal, & Scrivner, 1986), (Tester & M., 1997).

### Validation results

To check whether the model implementation was correct, the mean activity coefficient,  $\gamma_{\pm}$ , of solutions of NaCl and Na<sub>2</sub>SO<sub>4</sub> was calculated and compared with values found in Zemaitis et al. (1986). These solutions were of varying molalities, ranging from 0.01 to 4 mol/kg. The results obtained are displayed in Figures 1 and 2. As would be expected, the model yields mean activity coefficients that are quite close to the expected values for relatively low concentrations. However, as the concentration increases, the model displays slight deviations from the expected values.

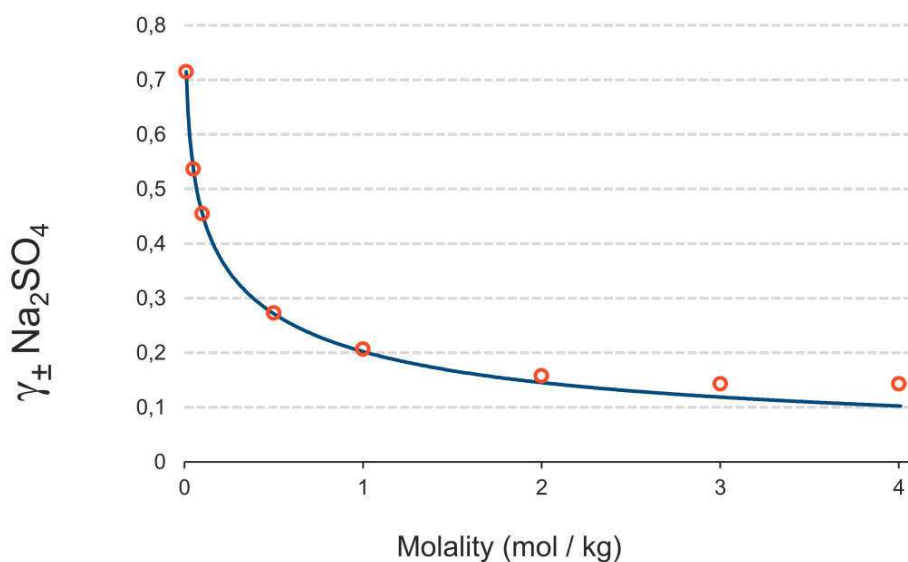


Figure 1 - Mean activity coefficient of Na<sub>2</sub>SO<sub>4</sub> solutions of varying molalities. The circles correspond to data extracted from Zemaitis et al. (1986).



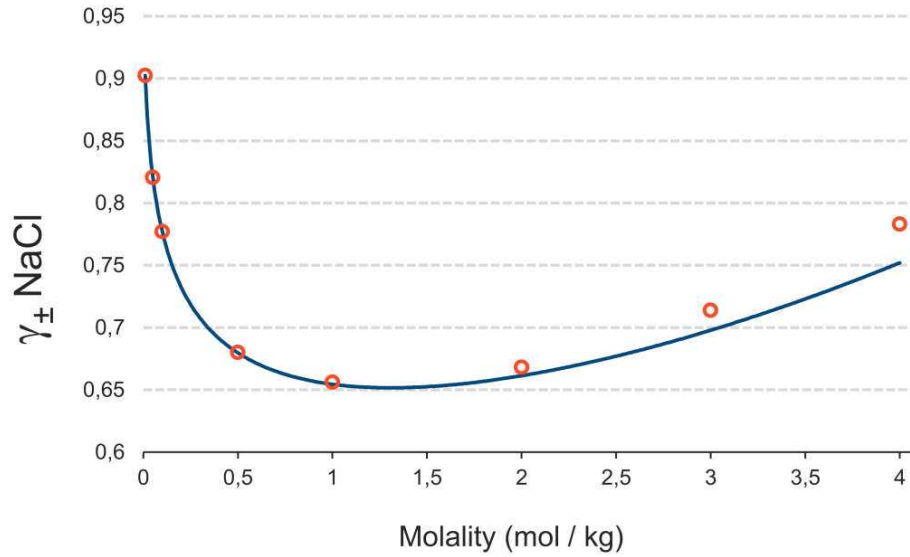


Figure 2 - Mean activity coefficient of NaCl solutions of varying molalities. The circles correspond to data extracted from Zemaitis et al. (1986).

### Temperature dependence of $K_{sp}$

In order to account for the effect of temperature on the solubility of burkeite the values of  $K_{sp}$  for both sodium sulfate and sodium carbonate were calculated from experimental solubility data (Linke & Seidell, 1965), (Shi & Ronald, 2001). Once these values were obtained, they were normalized with respect to the value corresponding to 115 °C, yielding relative values of  $K_{sp}$ . Mathematically:

$$K_{ps}^{relat}(T) = K_{sp}(T) / K_{sp}(115\text{ }^{\circ}\text{C}) \quad \text{EQ 2}$$

The values of relative  $K_{sp}$  of both sodium sulfate and are very close, especially for temperatures greater than 110 °C. These results are in accordance with what has been found by Wadsworth (2005). The graph displays decreasing values of relative  $K_{sp}$  (and, therefore, decreasing solubilities) for both salts, which is also to be expected from solubility data data (Linke & Seidell, 1965), (Shi & Ronald, 2001).

### Application-programming interface.

The WinGEMS block was developed through the Block Development Kit (BDK) application-programming interface (API), specifically designed to allow users to create their own specialized blocks. BDK consists of a collection of static libraries, header and source C++ files that, when compiled into a dynamic-link library (DLL), provide the subroutines to be called by the custom block.

For a WinGEMS block to be implemented, two files are necessary:

- a) **Block DLL:** the DLL generated by WinGEMS BDK upon compilation, encapsulating all subroutines involved in the calculations performed by the block. Most of the work involved in designing a block comes from generating this file.
- b) **WGB file:** a text file that specifies the target DLL to be sought by WinGEMS, the input labels made available to the user through the graphical user interface (GUI), as well as the input type and units, such as °C, cal/s, etc.

Upon initialization, WinGEMS reads the WGB file, which provides it with information on how to manipulate the DLL corresponding to the block (Figure 3). When a simulation is performed, WinGEMS calls the target DLL and reads its result as many times as required by the user.

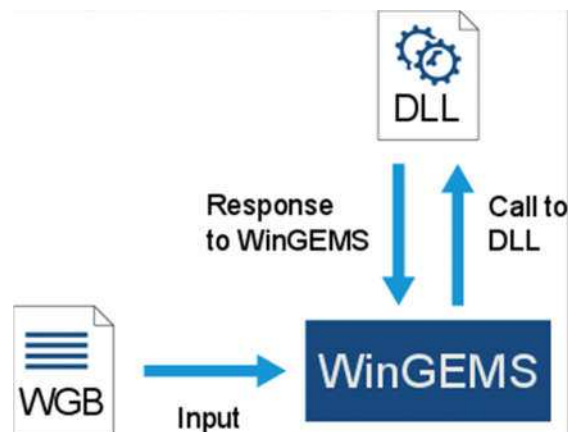


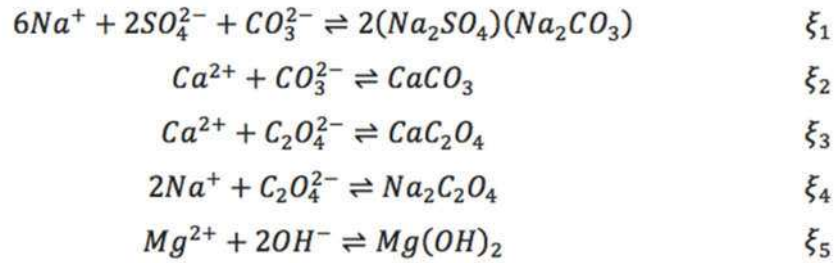
Figure 3 – WinGEMS reads the WGB file upon initialization. Once a simulation begins, it then calls the target DLL as many times as necessary.

## Equilibrium calculations

The solubilities of the following electrolytes are considered when performing calculations:

- Burkeite -  $2(\text{Na}_2\text{SO}_4)(\text{Na}_2\text{CO}_3)$
- $\text{CaCO}_3$
- $\text{CaC}_2\text{O}_4$
- $\text{Na}_2\text{C}_2\text{O}_4$
- $\text{Mg}(\text{OH})_2$

The equilibrium equations corresponding to the dissolution (or precipitation) of these compounds are the following.



The values  $\xi_i$  measure the advancements of each reaction. These reactions are associated to the following mass balances.

$$\begin{array}{l} m_{\text{Na}} = 6\xi_1 + 2\xi_2 \\ m_{\text{SO}_4} = 2\xi_1 \\ m_{\text{CO}_3} = \xi_1 + \xi_2 \\ m_{\text{Ca}} = \xi_1 + \xi_3 \\ m_{\text{C}_2\text{O}_4} = \xi_3 + \xi_4 \\ m_{\text{Mg}} = \xi_5 \\ m_{\text{OH}} = 2\xi_5 \end{array}$$

Since experimental data is available for burkeite precipitation, the burkeite calculations were conducted first and taken as the basis from which all other concentrations were found. These calculations allowed for the calculation of

$\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{Na}^+$  concentrations.

The concentrations of the remaining electrolytes were calculated using these values as inputs: from the concentration of  $\text{CO}_3^{2-}$ , the concentrations of  $\text{Ca}^{2+}$  was determined. The  $\text{Mg}^{2+}$  ions were treated separately and its solubility product was assumed constant due to lack of experimental data. No Pitzer parameters were found for calcium and sodium oxalate. For that reason, they were assumed not to precipitate. The ion pairs and trios whose binary and ternary interactions were considered are shown in Table 1.

Binary interactions	Ternary interactions
$\text{OH}^- - \text{CO}_3^{2-}$	$\text{OH}^- - \text{CO}_3^{2-} - \text{Na}^+$
$\text{OH}^- - \text{SO}_4^{2-}$	$\text{OH}^- - \text{SO}_4^{2-} - \text{Na}^+$
$\text{SO}_4^{2-} - \text{CO}_3^{2-}$	$\text{CO}_3^{2-} - \text{SO}_4^{2-} - \text{Na}^+$
$\text{Ca}^{2+} - \text{Mg}^{2+}$	$\text{Ca}^{2+} - \text{Mg}^{2+} - \text{SO}_4^{2-}$
	$\text{Na}^+ - \text{Mg}^{2+} - \text{SO}_4^{2-}$
	$\text{Na}^+ - \text{Ca}^{2+} - \text{SO}_4^{2-}$

Table 1 – Binary and ternary interactions considered in equilibrium calculations.

The following  $K_{sp}$  expressions were used:

$$K_{sp}^{Burkeite} = a_{\text{Na}}^6 a_{\text{SO}_4}^2 a_{\text{CO}_3}$$

$$K_{sp}^{CaCO_3} = a_{\text{Ca}} a_{\text{CO}_3}$$

$$K_{sp}^{Mg(OH)_2} = a_{\text{Mg}} a_{\text{OH}}^2$$

These  $K_{sp}$  data were calculated from (Green & Frattali, 1946) and directly extracted from (Plummer & Busenberg, 1981).

### Using the WinGEMS block

The model described above was implemented as a WinGEMS block that takes one stream as input and one stream. It does not modify the input stream in any way and displays its calculation results in the Current Values tab that can be found in the Edit block menu. The block reads the composition of the input stream and takes it as input for its calculations. The block is currently able to read the concentrations all components, except for that of  $\text{Mg}^{2+}$ , due to limitations of

WinGEMS BDK and that of  $\text{CO}_3^{2-}$ , which is not considered in WinGEMS. These have to be input manually in the Initial Values tab. It is crucial that the stream variables are set with the correct units. These are shown in Table 2.

Table 2 – Correct units in which the stream variables are to be set.

Stream variable	Unit
Temperature	°C
Carbonate	%mass of liquor
Hydroxide	%mass of liquor
Sulfate	%mass of liquor
Sodium	%mass of liquor
Magnesium	%mass of liquor
Calcium	%mass of liquor
Oxalate	%mass of liquor
Liquor flow	mt total/hr

Once the block is connected and calcium and oxalate concentrations are defined (if necessary), WinGEMS run normally.

## ANEXO B MILL CHARACTERIZATION

Table 1 – Mill sampling points and results

Samples extracted		Na	Ca	K	Mg	Mn	Ba	Al	Si	P	Cl	SO4	Total sulphur	CO3 (TOC/TIC)
	Values in black	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	g/l
Units	Values in Blue	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	
Wood chips	mg/kg DS	150	511	646	179	36,0	5,0	14	63,8	46	200			
Weak black liquor	mg/kg DS	49134	118	5360	30,4	7,2	1,96	152	6,62	30,5	620	6200		
Secondary condensates A	mg/l liquid	0,26	0,17	ND	ND	ND	0,005	0,09	2,65	<0,09	<2			
Secondary condensates B	mg/l liquid	ND	0,10	ND	ND	ND	0,01	0,06	0,58	<0,09	<2			
ESP-dust	mg/kg DS	248000	130	89000	34	17,2	<1	<10	64	20	<1		223600	
Weak liquor (Green liquor filtrate return)	mg/kg DS	5829	375	573	23,7	4,7	0,79	10,0	8,52	13,8	64			
Green liquor dregs									110,4	3000	700			
Green liquor (filtered)	mg/l	98000	6	9800	ND	ND	1,8	11,4	129,4	68,7	920	9500		
Lime	mg/kg DS	10598	672879	101	5551	128	146	220	429,6	10000	<100			
White liquor (unfiltered)	mg/l	113750	12375	12500	82	ND	3,2	15,6	140,0	69,6	950			
White liquor (filtered)	mg/l	115000	10	12000	ND	ND	13,4	12,0	255,1	16,9	870	16000	5610	
Mill Water	mg/l	6,7	2,9	0,57	1,3	0,01	0,01	0,13						0,00157
Lime mud (Filtered)														
Effluent from effluent treatment	mg/l	230	10	24	2,4	0,26	0,04	0,17	16,9	<0,09	200		238	
Digested pulp	mg/kg DS liq+pulp	235634	237	29834	736	45,0	6,0	111	102	120	1100			
Digested pulp carryover	mg/kg DS	104637	169	12779	622	33	2	65						
1st press brownstock	mg/kg DS liq+pulp	57552	552	7036	104	20,0	2,0	170	138	58	500			
2nd press brownstock	mg/kg DS liq+pulp	39156	448	4555	73	18,0	4,0	203	98	35	200			
3rd press brownstock	mg/kg DS liq+pulp	26923	412	3103	63	19,0	3,0	176	97	44	200			
1st pre bleach press	mg/kg DS liq+pulp	19379	382	2067	24	15,0	2,0	162	127	20	100			
2nd pre bleach press	mg/kg DS liq+pulp	4798	162	767	9	10,0	2,0	78	-	29	<100		6,0	
D0-press (out from)	mg/kg DS liq+pulp	1510	122	108	20	4,0	2,0	10						
EOP-press (out from)	mg/kg DS liq+pulp	3981	130	76	184	2,0	6,0	40						
D1-press (out from)	mg/kg DS liq+pulp	2165	71	45	177	1,0	4,0	29						
D2-stage filter (out from)	mg/kg DS liq+pulp	1219	36	22	164	0,6	3,0	20						
Final pulp	mg/kg DS	612	48	13	135	0,6	1,0	7						
Black liquor to digester	mg/kg D <sub>metals</sub>	23599	128	2596	11	3,2	1,13	11,5	11,3	21,2	360			44,2
Filtrate from 1st press brownstock	mg/kg D <sub>metals</sub>	18309	59	1793	7,6	1,91	1,14	9,35	4,9	13,2	200			29,3
Filtrate from 2nd press brownstock	mg/kg D <sub>metals</sub>	12214	39	1221	3,9	0,58	1,16	8,53	5,1	7,5	100			18,3
Filtrate from 3rd press brownstock	mg/kg D <sub>metals</sub>	7504	2	671	ND	ND	ND	4,74	3,5	3,4	51			9,2
Filtrate from 1st pre-bleach press	mg/kg D <sub>metals</sub>	4056	4,0	376	ND	0,59	0,79	7,12	2,1	2,0	47			2,8
Filtrate from 2nd pre-bleach press	mg/kg D <sub>metals</sub>	659	ND	54	ND	ND	ND	2,99	3,5	1,0	<2			0,64
Filtrate from D0-press	mg/l	170	14	15	1,7	0,3	0,06	0,49	0,5	1,16		910		0,42
Filtrate from EOP-press	mg/l	184	4,7	6,9	0,3	0,03	0,04	0,16	0,6	0,39		250	73,3	0,53
White water	mg/l	162	3,22	0,6	0,5	0,03	0,01	0,22	4,3			605		0,11

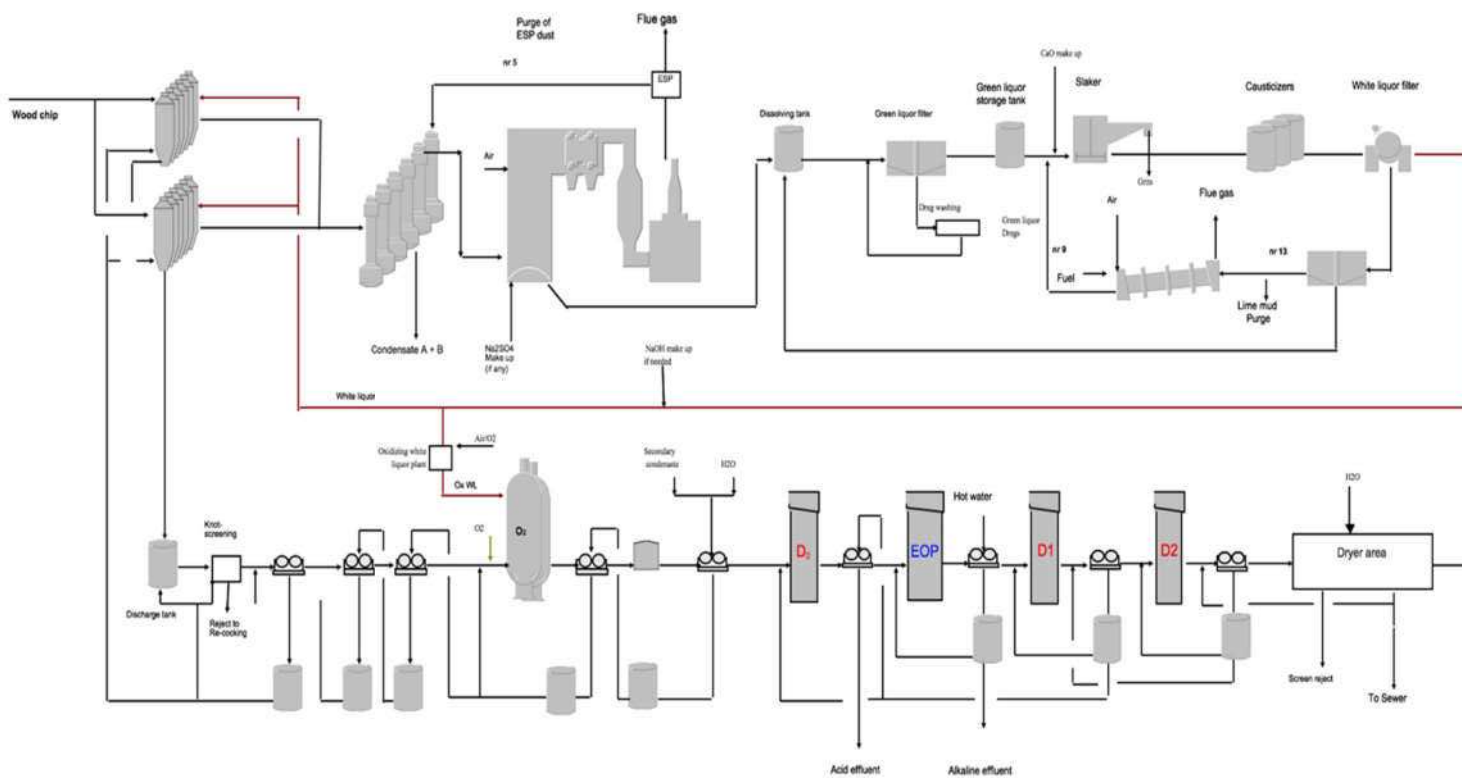


Figure 1 - WinGEMS Mill Model

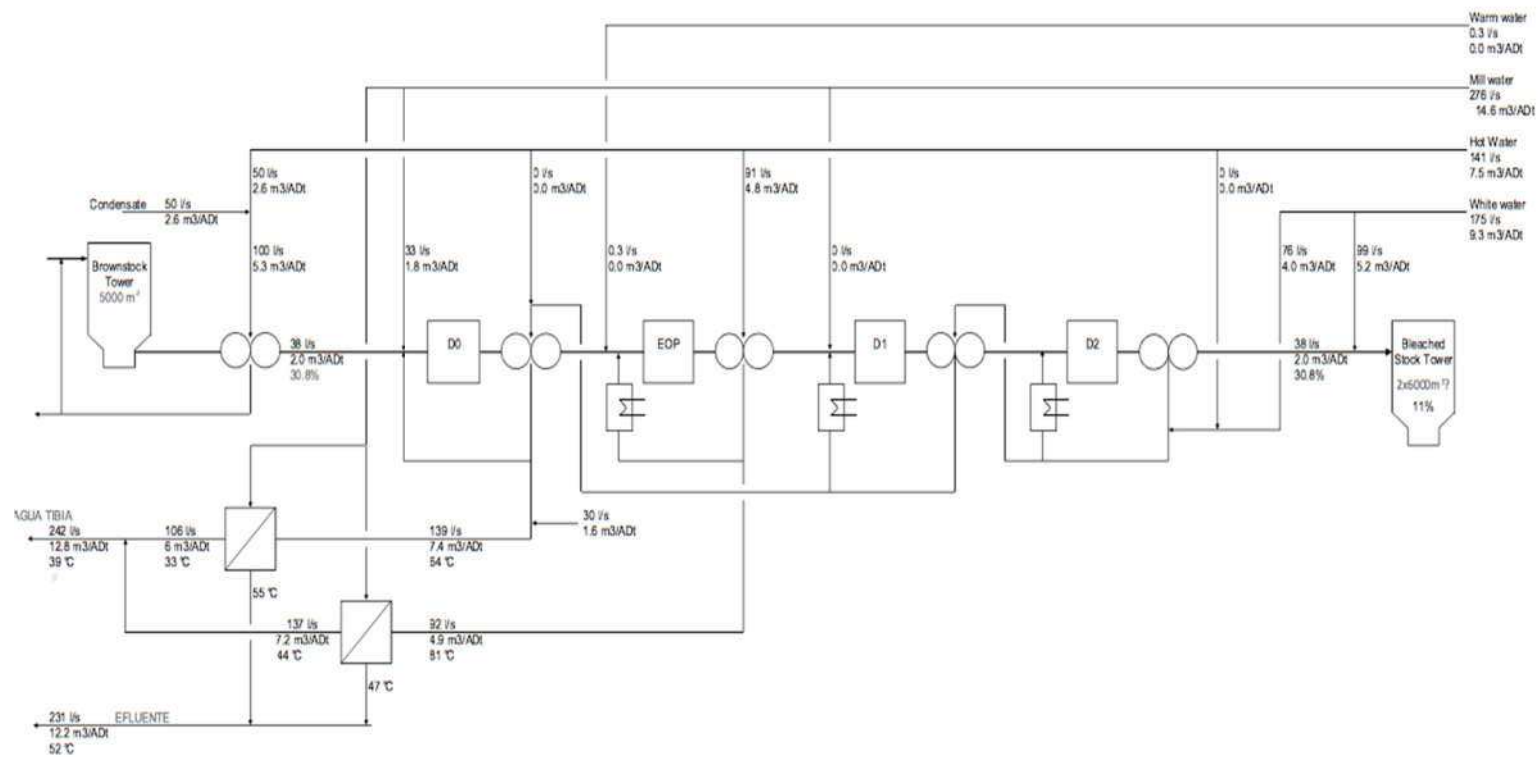


Figure 2 - Bleach plant water balance