WATER CONSUMPTION MINIMIZATION IN A BLEACH PLANT

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ABSTRACT

System closure in pulp and paper mills consists of optimizing internal reuse to reduce fresh water consumption. The bleach plant consumes the most water in the kraft process. Previous studies have shown that the impact of bleach plant closure on overall process performance can be modeled by WinGEMS and CADSIM simulators. Water minimization through recycling results in simultaneous buildup of non-process elements (NPEs). The NPEs accumulated in process streams lead to different operational problems in the bleach plant. Thus, an understanding of the fundamentals of NPE binding to pulp, their solubility in bleach filtrates, and their impact on the process is very important. This study presents a simulation tool for determination of overall mass and energy balance in a bleach plant, based on the knowledge of mill process data, aiming at reducing fresh water consumption through filtrate recycling. Furthermore, the NICA-Donnan Model was used to predict NPE (Mn^{2+}, Fe^{3+}, Mg^{2+}, Ca^{2+}) distribution. It was concluded that WinGEMS and CADSIM simulators are appropriate to describe the bleach plant process. Simulation of fresh water minimization was achieved by alkaline recycling (EOP) filtrate to the P washer to substitute fresh water, resulting in an average savings of 3.65 m^3 of fresh water/adt pulp. Although the reuse of (EOP) filtrate to wash P-stage pulp is not a common industrial practice, this concept was applied here since such filtrate had a low color in the bleach plant evaluated. The process simulations of the bleach plant presented in this study are satisfactory to describe the mill unit. The predicted results for the NICA–Donnan model compare quite well with the experimental data and were also successfully applied to describe specific and non-specific interactions between ions and fiber. The application of this methodology to reduce bleach plant fresh water consumption can lead to significant savings in process water use associated with new advanced technologies. The proposed methodology can also predict difficulties arising from NPE accumulation in the plants.

INTRODUCTION

System closure in pulp and paper mills consists of optimizing internal water reuse to reduce fresh water consumption and enhance energy and materials efficiency while respecting process constraints. Furthermore, the optimum closure target is specific to each mill because of great differences in process configurations. Significant gains can be made by implementing innovative closure strategies; process integration methods and applying tools for improving kraft process yield [1].

An overall reduction in the amount of fresh water required would lead to a decrease in the amount of wastewater generated. This led to the drive to maximize water recycling by closing the water loop. Water use reduction in the pulp mill starts with quantification of water consumption in the process stages, with attention focused on the stages with highest consumption, followed by introduction of process alternatives and continuous monitoring of each stage's performance [2]. The bleach plant is the main water consumer among the kraft process stages.

The first effort at closing a kraft process was at the Great Lakes Forest Products bleached kraft mill in Thunder Bay, Ontario in the mid-1970s. Later, Norrstrom *et al.* (1993) carried out a conceptual study of the closed cycle mill for the production of bleached chemical pulp [3].

However, water minimization through water recycle/reuse results in a simultaneous buildup of what are known as the Non-Process Elements (NPEs). The NPEs are those elements that play no part in the pulping and recovery processes. Their sources include wood chips; make-up lime; mill water and chemical reagents. NPEs will accumulate in process streams depending on their relative solubilities, which will lead to different problems including operational problems in the bleach plant [1]. Consequently, in order to predict NPE distribution in the mill processes it is necessary to understand fundamentals, such as element binding to pulp, element solubility in bleaching effluents, and process effects. Recent experiences have shown that these phenomena can be modeled by an existing modular simulator (WinGEMS and CADSIM) if fundamental models are carefully included in the simulation [2, 4].

This paper present the use of a simulation tool [2, 4] proposed for the determination of overall mass and energy balance in a bleach plant, based on the knowledge of mill process data. Furthermore, this study proposed to predict NPE distribution in a bleach plant using the NICA-

Donnan Model [5, 6, 7] and simulate process alternatives aimed at reducing water consumption through effluent recycle/reuse.

Simulation

Pulp and paper mills have progressed greatly over the years by applying conventional process analysis and engineering techniques. However, the kraft process is quite complex (large number of variables and streams) and the industry therefore uses computer simulation models to provide information on process performance and make processes changes.

Process simulation involves representing a chemical process through mathematical models. Model resolution defines the events that occur in the process. The goal of mill process simulation is total integration, aimed at improving mill performance without directly affecting the process, as for example, the reduction of water consumption.

In recent years many process simulation packages for steady-state and non-steady-state balances have been developed for the pulp and paper industry (Table 1). A number of studies have been carried out with these simulators aimed at reducing the amount of effluents from the bleach plant. Myers et al. (1989) used GEMS for optimum design and determination of oxygen delignification operating conditions in order to minimize delignification costs and reduce the total organic chlorine emissions from the bleach plant. Brooks et al. (1994) used simulation to evaluate the conversion of a conventional oxygen delignification softwood bleach plant to TCF bleaching based on hydrogen peroxide [1]. Other experiences in volatile organic compound (VOC) air emissions [1] and bleaching [2, 4] have shown that the effects of process details can be modeled by an existing modular simulator (WinGEMS and CADSIM) if fundamental models are carefully included in the simulation [2, 4].

For this study WinGEMS and CADSIM software were chosen to represent bleaching event simulation. NPE accumulation becomes an important factor when water consumption minimization is desired. This accumulation may negatively affect selectivity of bleaching reactions, product quality, tendency of deposit formation and corrosion in plant equipment. However, WinGEMS and CADSIM simulation results do not yet adequately predict NPE behavior and NPE concentrations can only be evaluated through simple mass balance [2]. Therefore, in the present study the complexity of NPE behavior has been included by using the NICA-Donnan thermodynamic model for simulation [7].

NICA-Donnan Model

Earlier attempts to describe the behavior of various metal ions in equilibrium were mainly based on their Langmuir isotherms. Concurrent determination of all necessary parameters for different ions at various pHs is needed, which is not an easy task. Recently, the Donnan equilibrium model was proven effective in describing ion exchange phenomena occurring between aqueous fibers and the exterior [9, 10].

The Donnan theory was initially developed to explain the distribution of ions over an impermeable membrane where thermodynamic equilibrium was assumed. Fiber slurries, which include the fiber phase and the liquid phase, can be treated as an electrochemical system due to the presence of ions. Thermodynamically, the system can be characterized by a combination of the chemical potentials of the phase constituents. The electrochemical potential of a solute ion *k* in the system can be presented as [5]:

$$\mu_k = RT\ln_k^0 + RT\ln m_k + RT\ln\gamma_k + z_k F\psi \quad (1)$$

where l_K^0 represents the standard state term, *R* is the universal gas constant, *T* is the Kelvin temperature of the system, m_K is the molarity of the ion, z_K is the valence of the ion, γ_K is the activity coefficient, *F* is the Faraday constant, and ψ is the electrical potential of the phase, or

$$\mu_k = \mu_k^0 + RT\ln m_\mu\gamma_\mu + z_k F\psi \quad (2)$$

where μ_K^0 represents the chemical potential of species *k* under standard conditions. The activity of species *k* is defined by $a_K = m_K\gamma_K$:

$$\mu_k = \mu_k^0 + RT\ln a_k + z_k F\psi \quad (3)$$

Table 1-Pulp and Paper simulators [8]

Simulation pakages	Institution
FlowCalc - Flowsheet Calculus	*Simulation Software*
WinGEMS 5.3 - General Energy and Material Balance System	*Department of Chemical Engineering University of Idaho; Pacifc Simulation* http://www.pacsim.com
MAPPS - Modular Analysis of Pulp and Paper Systems	*Institute of Paper Science and Technology*
MASSBAL - Mass and Energy Balance	*SACDA Inc. (Systems Analysis Control and Design Activity) e Open Models Inc.* http://www.openmodels.com
ASPEN PLUS - Advanced System for Process Engineering	*Aspen Technology, Inc.* http://www.aspentech.com
CADSIM PLUS, PAPDYN	*Aurel System Inc.* http://www.aurelsystem.com

The difference of the electrochemical potential of species *k* having a valence of z_K in two phases, including the pressure term for the solution will be:

$$\mu_k'' - \mu_k' = z_k F\left(\psi'' - \psi'\right) + RT \ln \frac{a_k''}{a_k'} - \int_{P}^{P^0} \nabla_k dP \quad (4)$$

Superscripts ‘ and ‘’ represent the fiber and aqueous phases, respectively. P is the pressure in the fiber phase, P^0 is the pressure in the aqueous phase, and ∇_K is the partial molar volume of ion k. Since the fiber wall is highly porous the osmotic pressure differential required for the transfer of the mobile ions between phases would be negligible [5]. If this is the case the last term of Eq. (4) can be neglected. At equilibrium $\mu' = \mu''$, and Eq. (4) can be simplified to

$$z_k F\left(\psi'' - \psi'\right) + RT \ln \frac{a_k''}{a_k'} = 0$$

or

$$-z_i F\left(\psi'' - \psi'\right) = RT \ln \frac{a_k''}{a_k'} \quad (5)$$

or

$$-F \frac{\left(\psi'' - \psi'\right)}{RT} = \frac{1}{z_i} \ln \frac{a_k''}{a_k'}$$

The left-hand side of Eq. (5) is a constant, which can be designated ln(*λ*). *Λ* is known as the distribution coefficient of species *k* in the fiber slurry. Eq. (5) can be rearranged as shown below:

$$\lambda = \left[\frac{a_k''}{a_k'}\right] = \left[\frac{\gamma_k'' m_k''}{\gamma_k' m_k'}\right]^{\frac{1}{z_k}} \quad (6)$$

The activity coefficients approach unity $\left(\gamma'' = \gamma' = 1\right)$ when the ionic strength of the liquid phase is less than 10 mM [5]. In our study the ionic strength, which is less than 3 mM, is much lower than this limit. When the activity coefficients approach unity the distribution coefficients of all species can be calculated from the concentration in the two phases:

$$\lambda = \left[\frac{m_k''}{m_k'}\right]^{\frac{1}{z_k}} \quad (7)$$

However, Donnan-type models account for nonspecific interaction. Pulp systems are quite complex and there is evidence that metal ions in fibers do not have the same chemical environment as those in solution, which is evidence for specific metal–fiber interactions. A Donnan-type model for nonspecific binding of ions combined with the non-ideal competitive adsorption (NICA) equation for specific binding, known as the NICA–Donnan model, is available. This approach, which combines a continuous distribution of affinity constants and a Donnan phase, has been successfully applied to calculate specific interactions of proton or metal and functional groups in the lignin/fiber.

Recently, Bouanada et al. (2002) employed the NICA–Donnan model to satisfactorily predict acid/base properties of a lignocellulose substrate. Dupont et al. (2003) studied the sorption properties of a lignocellulose substrate toward lead, copper, and cadmium [7].

The partitioning of proton or metal ions between the lignocellulose material (lignin or fiber) and the external solution (or liquor) is described by considering the equilibrium, electroneutrality, mass balance relationships and binding of proton or metals with the various functional groups in the lignin/fibers. This approach combines chemical heterogeneity and electrostatic effects. Proton or metal binding to lignin/fiber is assumed to occur with specific interactions between the cation and the negatively charged surface functional groups through nonspecific electrostatic binding to any residual negative charge. Specific binding is described by the NICA equation, and nonspecific binding is expressed by the Donnan equation.

The NICA equation is employed for the specific binding relationship between a proton or metal ion and a functional group on the lignin/fiber. The NICA equation assumes a continuous distribution of site affinities. It allows that the affinity distributions for a proton and the various metal ions not only have different median affinities for each ion, but also have ion-specific non-ideality or heterogeneity. The proton or metal ion binding to each site of type S at the sorbent is described by the reaction:

$$S^- + M^{z+} = SM^{(z-1)+} \quad (8)$$

where M^{z+} is a cation of charge z+, and S- and $SM^{(z-1)+}$ are surface species. The total fractional surface coverage of component i is expressed by the integral equation

$$\theta_{i,T} = \int_{\Delta \log K_i} \theta_{i,L} f(\log K_i) d(\log K_i) \quad (9)$$

Where f(logK_i) is the distribution function of the affinity constant, K_i, $\theta_{i,L}$ is the local adsorption isotherm, the isotherm for binding of ion i to a group of identical sites; and $\Delta \log Ki$ is the range of logKi considered. Koopal et al. [7] derived the mono-modal form of the NICA equation. Usually there are two major types of sites in the affinity distribution for the binding of protons or metal ions to lignin/fiber, considered to be due to carboxylic-type groups and phenolic-type groups, respectively. The NICA equation in its thermodynamically consistent version is

$$\begin{aligned} Q_i = & Q_{\max,1} \frac{n_{i,1}}{n_{H,1}} \frac{(K_{i,1} c_{D,i})^{n_{i,1}}}{\sum_j (K_{j,1} c_{D,j})^{n_{j,1}}} \\ & \times \frac{\left[\sum_j (K_{j,1} c_{D,j})^{n_{j,1}}\right]^{p_i}}{\left[1 + \sum_j (K_{j,1} c_{D,j})^{n_{j,1}}\right]^{p_i}} \\ & + Q_{\max,2} \frac{n_{i,2}}{n_{H,2}} \frac{(K_{i,2} c_{D,i})^{n_{i,2}}}{\sum_j (K_{j,2} c_{D,j})^{n_{j,2}}} \\ & \times \frac{\left[\sum_j (K_{j,2} c_{D,j})^{n_{j,2}}\right]^{p_i}}{\left[1 + \sum_j (K_{j,2} c_{D,j})^{n_{j,2}}\right]^{p_i}} \end{aligned} \quad (10)$$

where subscripts 1 and 2 refer to the carboxylic- and phenolic-type parts of the distribution, respectively; subscript H refers to the proton; Q_i is the total amount of component i bound to the surface species of the lignin/fiber (in mol kg^{-1}); Q_{max} is the number of sites (in mol kg^{-1}); K_j is the median affinity constant for component j; and $c_{D,j}$ is the local concentration of component j near the binding sites (in mol L^{-1}). The various summations are over all j components. This includes the proton and all metal ions present. The relationship between $c_{D,j}$ and the concentration of component j in the aqueous phase (c_j) is determined by a Boltzman factor, which depends on the local electrostatic potential in the lignin phase. The Donnan model is used to calculate $c_{D,j}$ as shown in by Donnan Equilibrium. The parameter ni accounts for the "non-ideal" behavior (n≠1, non-ideal; n = 1, ideal) of component i. For ion adsorption, n_i takes values of 0<n≤1. The value of p (0<p≤1) determines the width of the distribution due to the intrinsic chemical heterogeneity of the sorbent and is the same for all components. The total number of sites, $Q_{max,1}$ and $Q_{max,2}$, are expressed as the sum of the concentration of all the surface species:

$$\begin{aligned} Q_{\max,1} &= Q_{S1} + Q_{H1} + \sum Q_{M_j,1}, \\ Q_{\max,2} &= Q_{S2} + Q_{H2} + \sum Q_{M_j,2}. \end{aligned} \quad (11)$$

Here subscripts 1 and 2 refer to the two-component distribution; Q_S is the number of sites in the free state, S^- (free of bound ions); Q_H is the number of protonated sites; and $\sum Q_{M_j}$ is the

number of sites occupied by cation, M^{z+}. Thus, the net charge of the lignin/fiber, q (in Eq kg^{-1}) is given by the charge contributions from the various surface species of the two distributions, with

$$q_1 = -Q_{\max,1} + Q_{H1} + z\sum Q_{M_j 1},$$

$$q_2 = -Q_{\max,2} + Q_{H2} + z\sum Q_{M_j 2}, \quad (12)$$

$$q = q_1 + q_2.$$

In the absence of metal ions, Eq. (10) becomes

$$Q_H = Q_{\max,1}\frac{(K_{H,1}c_{D,H})^{m1}}{1+(K_{H,1}c_{D,H})^{m1}} + Q_{\max,2}\frac{(K_{H,1}c_{D,H})^{m2}}{1+(K_{H,1}c_{D,H})^{m2}} \quad (13)$$

where Q_H (mol/kg sorbent) is the number of protonated sites, subscript H refers to protons, and $m = n \times p$.

For non-specific binding interactions (Donnan equilibrium) the lignin/fiber is regarded as an electrically neutral homogeneous phase, which is separated from the external solution. The presence of fixed charged functional groups on the lignin/fiber induces a Donnan equilibrium, and as a result, the concentrations of free cations inside and outside the lignin/fiber phase are not equal. This Donnan phase has a particular volume throughout which there is a uniform, averaged electrostatic potential known as the Donnan potential, ψ_D. The volume of the Donnan phase can be related to the swelling properties of the lignin/fiber suspensions. The Donnan equilibrium expression is [7]

$$c_{D,j} = \lambda^{z_j} c_j, \quad (14)$$

where $c_{D,j}$ is the molar concentration of the cation or anion j present in the Donnan phase and z_j is its charge, c_j is the molar concentration of the cation or anion j present in the bulk solution, ë refers to the Donnan equilibrium constant, and its relationship with the Donnan potential is

$$\lambda = \exp(-e\psi_D / kT), \quad (15)$$

where e is the charge on the electron and k is Boltzmann's constant. It is assumed that the Donnan volume value depends on the strength according to the equation:

$$\log V_D = b(1 - \log I) - 1 \quad (16)$$

where I is the ionic strength, and b is an adjustable parameter [7].

The electroneutrality of the Donnan phase and the external bulk solution are expressed by:

$$q / V_D + \sum_j z_j c_{D,j} = 0,$$

$$\sum_j z_j c_{D,j} = 0, \quad (17)$$

where q is the net charge of lignin substance, V_D is the volume of water in the Donnan phase (L kg-1), $c_{D,j}$ is the molar concentration of the cation or anion j present in the Donnan phase and z_j is its charge, and c_j is the molar concentration of the cation or anion j present in the bulk solution.

The expression for the ionic mass balance in the solution is

$$n_j = c_{D,j}V_D + c_j (V - V_D) \quad (18)$$

where n_j is the total mole number of ion j, and V is the total volume of the solution (L). By use of the previous equations, the partitioning of proton or metal ions between the sorbent and external solution in an aqueous suspension can be obtained.

With the above proton binding parameters, the NICA–Donnan model requires calculation of six parameters. These are the total site densities: $Q_{max,\ 1}$ and $Q_{max,\ 2}$; the median protonation constants (K_1 and K_2); and the non-ideality–generic heterogeneity parameters (m_1 and m_2). Subscripts 1 and 2 refer to carboxyl and phenolic functional groups. These parameters can be estimated from the regression of the surface charge values which are obtained from potentiometric titration data for lignin/fiber suspensions [9]. The Donnan equilibrium, mass balance, and electroneutrality equations are used to obtain the surface charge values [7].

After obtaining the above proton parameters, the interactions between metal ions and the lignin/kraft fiber are calculated, and the metal binding parameters are obtained. These parameters are binding constants of metal *i* ($K_{i,1}$ and $K_{i,2}$), ion-specific non-ideality parameters ($n_{i,1}$ and $n_{i,2}$), and intrinsic heterogeneity parameters (p_1 and p_2). The parameters p_1 and p_2 are the same for all metal ions binding to a specific sorbent. Here, the p_1 and p_2 values obtained by fitting the binding data of a certain metal ion are used directly in the binding calculation of other metal ions, and do not need to be fitted. Given the above parameters of single-metal ion binding, the binding relationship between the mixed metal ions and the lignocellulose substrate/kraft fiber can be predicted.

Summarizing, the NICA–Donnan model has proven its value in practice for the description of metal ion binding to various sources of dissolved and dispersed organic matter. Its present day use is also greatly facilitated by the computer programs FIT of Kinniburgh, ECOSAT of Keizer and Visual MINTEQ of Gustafsson. *FIT* is a computer program for fitting models to data by non-linear regression. It is especially designed to calculate optimal parameter values for adsorption isotherms. *ECOSAT* is a computer program that can be used to calculate the chemical equilibrium composition of soil–water systems. It contains a whole range of adsorption models including the NICA–Donnan model.

In the present study, the Visual MINTEQ software was chosen to represent the complexity of NPE behavior during the simulations.

EXPERIMENTAL

In the present study, an elemental chlorine free (ECF) eucalyptus kraft pulp bleach plant was used as the model system (Figure 1). A five-stage bleaching sequence, OD(EPO)DP, was considered: oxygen delignification (O); chlorine dioxide (D); peroxide and oxygen extraction (EPO); chlorine dioxide (D); hydrogen peroxide (P).

Basic requirements for simulation

The flow diagram was developed using the block library and dynamic link libraries, of WinGEMS and CADSIM simulators, respectively. Some simplifications were made and the flows, which do not interfere with mass and energy balances were removed. Input data for WinGEMS and CADSIM simulation, were collected in the mill unit. These data were acquired through computational programs installed in the control process and organized into an electronic Excel spreadsheet and were transmitted to WinGEMS and CADSIM simulators by executable routines programmed in Visual Basic and C^+ computer languages, respectively.

Data collection

For simulation of the bleach plant, about 25 data sets, containing about 5 variables per set were collected at the mill (Table 2), over a period of six months for a total of 2.512 daily averages for each variable. Data collected during start-up operations and unstable operating conditions were removed from the database to avoid mass and energy balance errors.

Furthermore, to better understand the bleach plant and to acquire more detailed process information, pulp and filtrate samples were collected and analyzed using standard procedures.

Data and the information entry to the WinGEMS and CADSIM models involves solving mass and energy process balances through interactive calculus. For the WinGEMS simulator, the simulation stops when the convergence criterion is reached whereas for CADSIM, the simulation is dynamic. Following, the results for each bleach plant variable are organized automatically into Excel spread sheets.

Measurements made on mill samples were compared to predicted values to validate the simulation model.

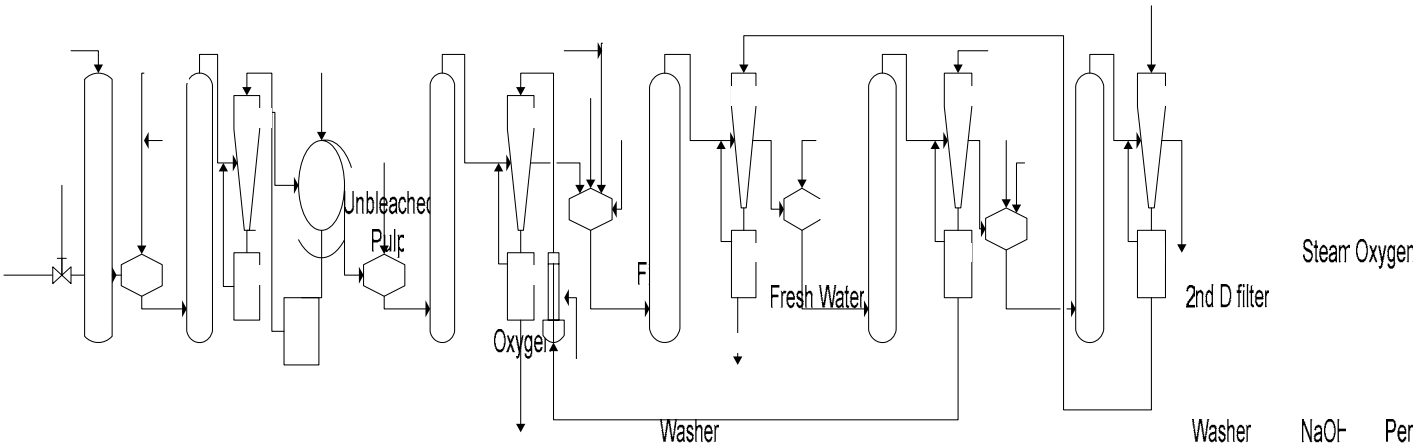

Figure 1 - The bleach plant.

NPEs prediction

Increased concentrations of NPEs in different process streams will lead to different problems, including: increased corrosion; plugging; deposit formation; lime cycle accumulation; operational problems in the bleach plant and adverse environmental impacts. Elements most responsible for bleach plant problems are: Mn^{2+} and Fe^{3+} that favor the degradation of peroxide in the bleaching stage; Mg^{2+} and Ca^{2+} that can accumulate and form leave insoluble deposits and plug in tubes and equipment.

The NICA-Donnan Model was used to predict NPEs distribution (Mn^{2+},Fe^{3+}, Mg^{2+},Ca^{2+}) in a bleach plant. The *Visual MINTEQ* software was used to facilitate simulation of the behavior of these complex elements.

Given the complexity of the bleach plant and NPE distribution, it was necessary to adopt the Visual MINTEQ software as a computational tool. The Visual MINTEQ software is a version of MINTEQA2, which was released by the USEPA (United States Environmental Protection Agency) in 1999 as a chemical equilibrium model for the calculation of metal speciation, etc. for natural waters.

Table 2-Variables of the bleach plant

Sets	Variables
Unbleached pulp	Flow (m^3/h); Kappa Number; consistency (%); temperature (°C)
Oxygen-O stage	Flow (m^3/h); pressure (bar); temperature (°C)
NaOH-O stage	Flow (m^3/h)
Steam-O stage	Flow (kg/h); pressure (bar)
Pulp- O stage	Flow (Air-dried/h); Kappa number; consistency (%); temperature (°C); pressure (bar)
Filtrate-O stage	Flow (m^3/h); pH
Fresh water-washer O stage	Flow (m^3/h)
Dioxide Chlorine-D stage	Flow (m^3/h)
Pulp-D stage	Temperature (°C); pH
Filtrate-D stage	Flow (m^3/h); pH
NaOH-EPO stage	Flow (m^3/h)
Peroxide-EPO stage	Flow (m^3/h); temperature (°C)
Steam-EPO stage	Flow (kg/h); pressure (bar)
Oxygen-EPO stage	Flow (m^3/h); pressure (bar); temperature (°C)
Pulp-EPO stage	Temperature (°C); pH; Kappa Number
Filtrate-EPO stage	Flow (m^3/h); pH
Dioxide Chlorine-2nd D stage	Flow (m^3/h); pressure (bar); temperature (°C)
Pulp- 2nd D stage	Temperature (°C)
Dryer water	Flow (m^3/h); temperature (°C); pH
Filtrate-2nd D stage	Flow (m^3/h); pH
Peroxide-P stage	Flow (m^3/h); temperature (°C)
NaOH- P stage	Flow (m^3/h)
Pulp- P stage	pH
Fresh water-washer P stage	Flow (m^3/h)
Filtrate-P stage	Flow (m^3/h); pH

Visual MINTEQ has been developed to make the features of MINTEQA2 more readily accessible and it includes several options for adsorption and metal-organic matter complexation modeling (NICA–Donnan).

This software was integrated with CADSIM Plus simulator. CADSIM Plus was implemented through an executable routine programmed in C^+ computer language. It was not possible to establish a computational interface between this software and the WinGEMS simulator, because this program is not compatible with this simulator.

Water consumption minimization

In this study the fresh water consumption minimization was made through the possible reuse the discharge filtrates, to substitute the fresh water used in the bleach plant. For this study, the fresh water is used in the 1st D and P washers. Also, the 1st D and EOP filtrates had been identified as the only ones not reused in the bleach plant. The substitution of the fresh water for the 1st D filtrate in the washer of the O stage, is impracticable because probably it would cause problems, therefore the filtrate of this washer is sent for the recovery cycle. Thus, the substitution of the fresh water for the EOP filtrate in the washer of the P stage was fresh water consumption minimization in the bleach plant (Figure 12). Furthermore, a NPEs distribution simulation was after made the substitution of the fresh water for this filtrate.

RESULTS AND DISCUSSION

WinGEMS and CADSIM validation

Figure 2 compares measured and simulated values for kappa number, brightness, and filtrate pH (Figure 2) using WinGEMS while Figure 3 compares filtrate flow, pulp temperature and consistency for and CADSIM.

As observed in Figures 2 and 3, simulated values are in close agreement with measured values. This was confirmed by low values of the relative average error (RAE) of these variables. The relative average error (RAE) is defined by equation:

$$\mathrm{ERM} = \frac{1}{N}\sum_{i=1}^{N}\frac{\left|y_{real} - y_{simulation}\right|}{y_{real}} \quad (18)$$

y_{real} is the mill value and $y_{simulation}$ is the values predicted for the CADSIM and WinGEMS simulators; N is the number of data [13].

For kappa number an error of 10.57% was found, that is justified by the absence of models to predict the performance of this variable in the simulation. For brightness, errors of 1.95%, 5%, 1.75%, 0.46%, 1.42% and 0.21%, were found for successive bleaching stages. Although quantitative differences exist, the predicted values are satisfactory from a computational point of view (Figure 2). For the other variables, filtrate flow, filtrate pH, pulp temperature and consistency, RAE's were below 1%.

Based on these results, it is concluded that WinGEMS and CADSIM simulators can adequately describe the bleach plant and determine mill process performance variables.

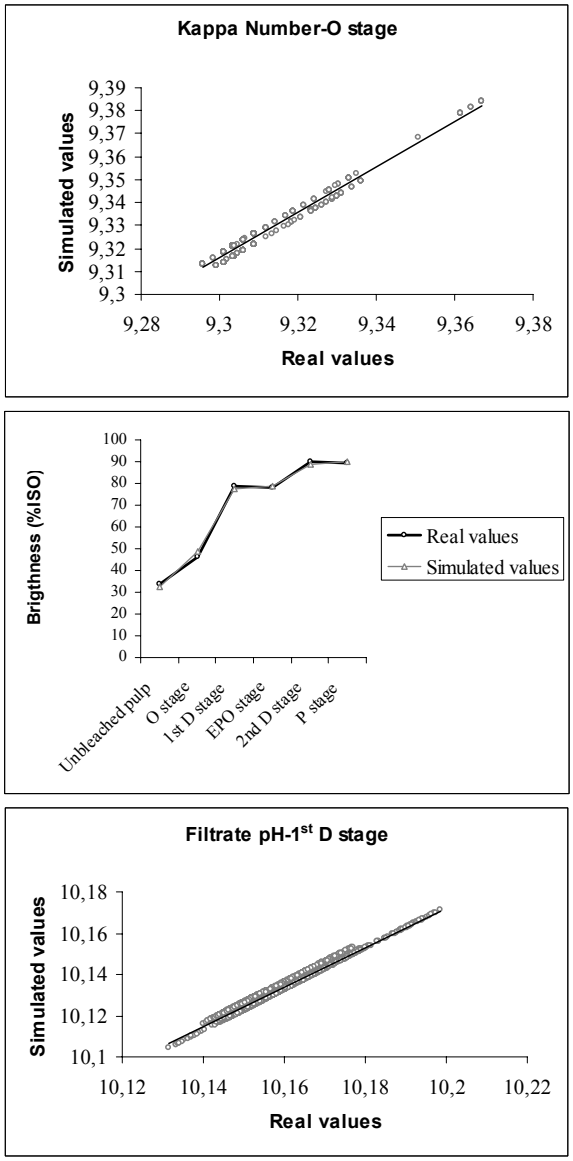

Figure 2 - Comparison between the mill values and the values predicted for the WinGEMS simulator.

NPEs: concentration and distribution

Initially, the NICA–Donnan model was employed to calculate ion binding to fiber under mill operating conditions (pH, flow and temperature).

Potentiometric titration data for unbleached pulp, oxygen delignification, chlorine dioxide; peroxide oxygen extraction and hydrogen peroxide pulps were based on literature values [7,9,11] and were converted into surface charges on the fibers in the suspensions through the thermodynamic model, and pH relationship by use of Donnan equilibrium, mass balance, and electroneutrality equations [12].

The NICA–Donnan model was employed to describe the interactions between Mn^{2+},Fe^{3+}, Mg^{2+},Ca^{2+} and fibers in O stage (Figure 4), 1st D stage (Figure 5), EPO stage (Figure 6), 2nd D stage (Figure 7) and P stage (Figure 8).

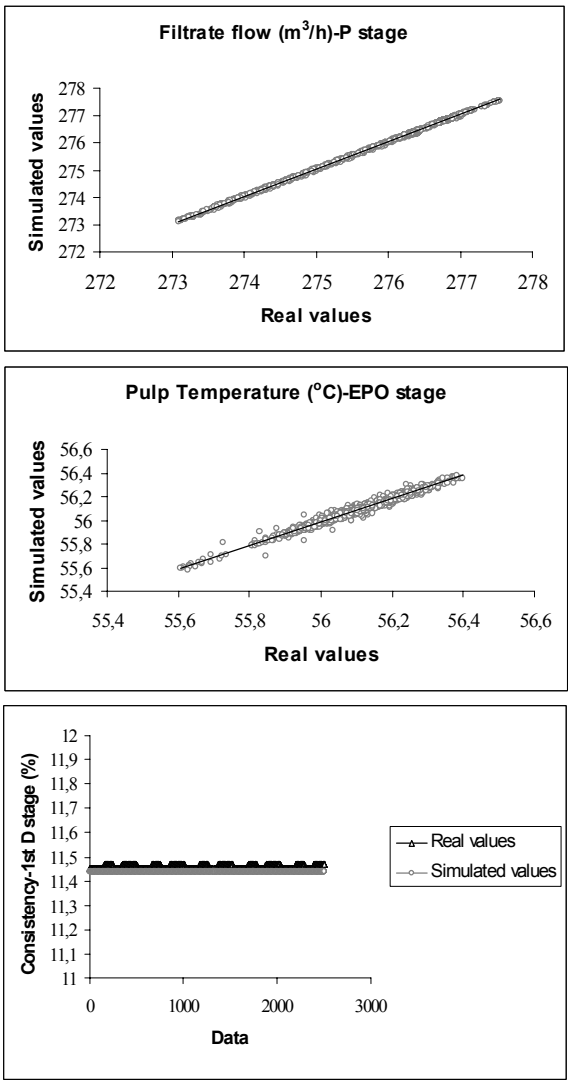

Figure 3 - Comparison between the mill values and the values predicted for the WinGEMS simulator.

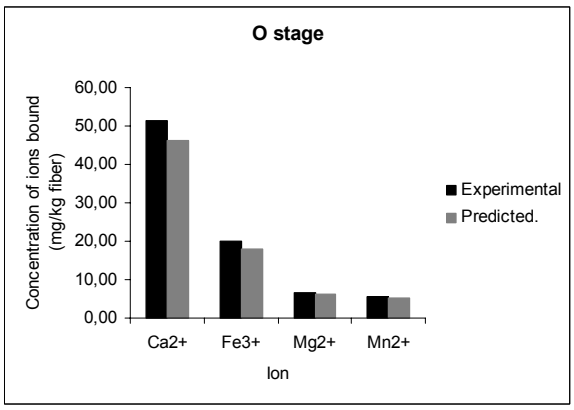

Figure 4 - Comparison of ions predicted and experimental data: O stage.

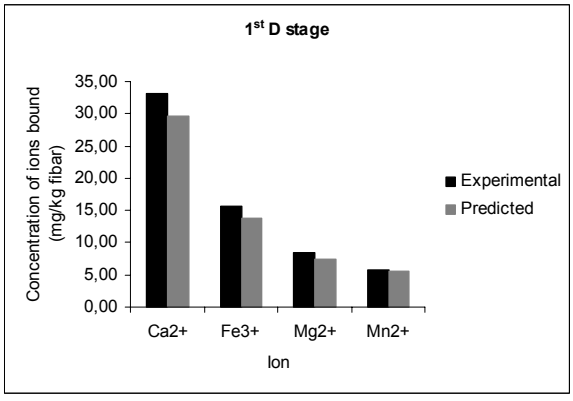

Figure 5 - Comparison of ions predicted and experimental data: 1st D stage.

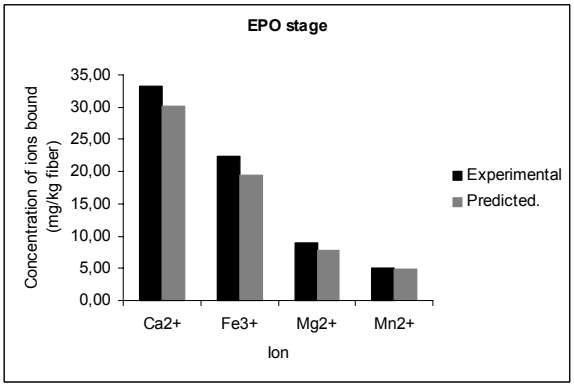

Figure 6 - Comparison of ions predicted and experimental data: EPO stage.

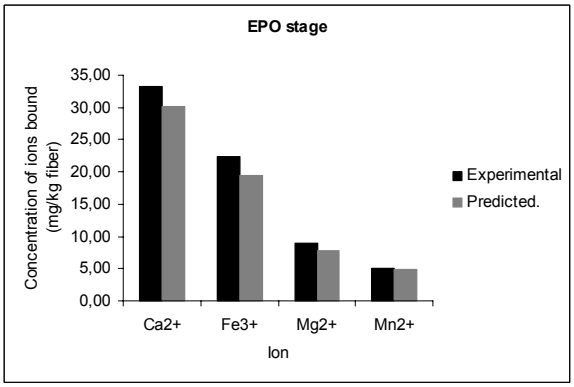

Figure 7 - Comparison of ions predicted and experimental data: 2nd D stage.

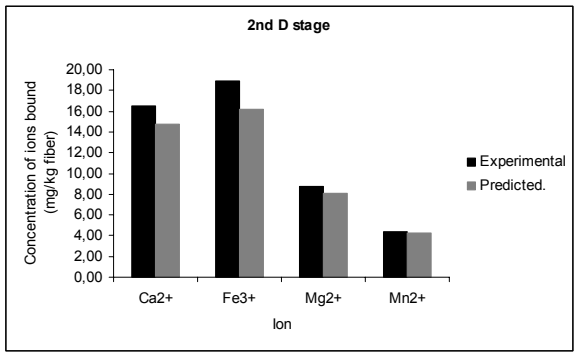

Figure 8 - Comparison of ions predicted and experimental data: P stage.

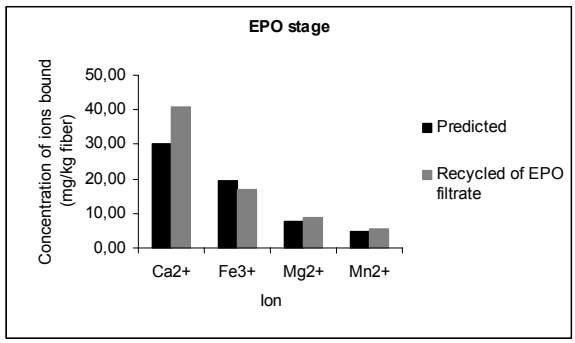

Figure 9 - Comparison of ions predicted in EPO filtrate before and after EPO filtrate recycle.

As shown in Figures 4-8 there was a satisfactory agreement between predicted and experimental data. The largest errors were found for Fe^{3+}ion: 14, 9% for O stage pulp and 14,1% for 1st D stage pulp. For Ca^{2+} errors of 10,9% were found for 2nd D stage pulp and 6, 3% for P stage pulp. For Mg^{2+}, errors of 12% for EPO stage pulp and 7, 4% for 2nd D stage pulp were found. The lowest errors were for Mn^{2+} ion, 4% for P stage pulp and 2,5% for 1st D stage pulp.

Fresh water reduction

The simulation of fresh water consumption reduction was made using alkaline filtrate (EPO) in the P washer to substitute the fresh water used in this stage (Figure 11). Simulation of this alternative resulted in an average savings of 219 m^3/h of fresh water, equivalent to an economy of 74% of the flow.

Simulation of NPE concentrations after alkaline filtrate reuse was also done. After recycle, EPO filtrate (Figure 9) and 2nd D stage filtrate (Figure 10) were most affected. For the other bleaching stages changes in NPE concentrations were below of 1%. For the EPO stage, increases in the concentrations of 36%, 15%, 12% were found for Ca^{2+}, Mn^{2+} and Mg^{2+}, respectively together with a decrease of 12% in Fe^{3+} concentration. In the 2nd D stage, reductions of 3% and 2% were found for Ca^{2+} and Mn^{2+}, respectively.

The mill implementation of this alternative would require special attention to the observed increase of manganese in the EPO stage and calcium in the D_1 stage that could cause serious operational problems.

It should be noted that in this part of the study only simulations were made, without mill measurements to validate them. This validation should be the focus of future research.

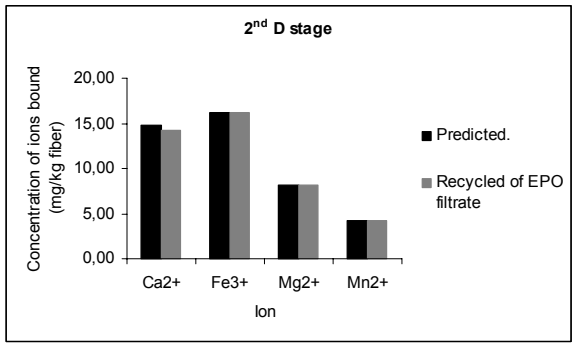

Figure 10 - Comparison of ions predicted in the 2nd D stage before and after EPO filtrate recycle.

CONCLUSIONS

- The bleach plant process simulations presented in this study are consistent and satisfactorily describe the mill unit. This conclusion is further corroborated by comparisons between measured and simulated values. These simulations also allow a more detailed analysis of the bleach plant, including determination of bleaching variables and visualization of the complexity of the process without making direct changes.
- In this study, the NICA–Donnan equation was employed to describe the binding of NPEs (Mn^{2+},Fe^{3+}, Mg^{2+},Ca^{2+}) in the bleach plant. The predicted results compare quite well with experimental data. The equation was also successfully applied to describe ion (Mn^{2+},Fe^{3+},Mg^{2+},Ca^{2+})–fiber interactions. It is noted that the NICA–Donnan model accounts for nonspecific as well as specific interaction between ions and organic matter. Thus, it is consistent with the observed physical behavior of ion–organic matter interactions.
- The application of the simulation methodology to study fresh water consumption reduction in a bleach plant can contribute to significant savings in water use. This economy is associated with new advanced technologies that include reduction in effluent generated in the

bleaching process. The methodology developed also deals with difficulties faced in the plants due to NPE accumulation. Through the integration of tools developed in this study, water minimization and reuse limits can be established bleach plants, considering their individual needs specificities.

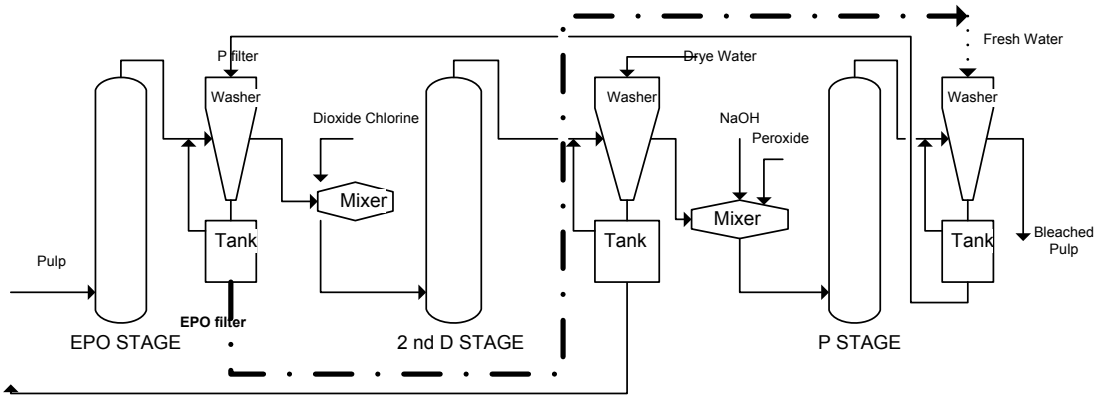

Figure 12 – Recycled of EPO filtrate in the washer of P stage.

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