

Selective removal of chloride and potassium in kraft pulp mills

LICÍNIO MANUEL G.A. FERREIRA, MICAELA A.R. SOARES, ANA PAULA V. EGAS, AND JOSÉ ALMIRO A.M. CASTRO

ABSTRACT: Chloride (Cl) and potassium (K) are nonprocess elements (NPEs) that can accumulate to high levels in highly closed pulp mills and cause serious problems, particularly in the recovery boiler operation. Based on data from two pulp mills, we collected the following information for Cl and K: the chemical composition of precipitator ash where these two NPEs are accumulated, input and output mass flow streams entering and leaving the process, and the corresponding enrichment factors. To identify the best process to minimize this accumulation, we evaluated direct purge, leaching, evaporation/crystallization, and ion-exchange techniques. Using one of the pulp mills as a reference, we performed computer simulations to study how the sticky temperature of the ashes varies with the amount treated. A preliminary economic analysis led to the conclusion that the leaching and the ion-exchange techniques were the more attractive alternatives for treating ash collected from the electrostatic precipitator.

Application: Mills can use the information from this research to help address boiler-plugging problems caused by high levels of chloride and potassium.

Kraft pulp mills have progressively implemented better measures of closing process streams and potentially minimizing the generation and discharge of toxic contaminants. Further progress in mill closure is hampered by the accumulation of nonprocess elements (NPEs), especially chloride (Cl) and potassium (K). High concentrations of these elements lower the melting point of the deposits that stick on recovery boiler tubes. The deposits plug flue gas passages, thus decreasing boiler capacity.

Since chloride and potassium are enriched in the ashes of the boiler, most of the processes proposed in the literature have been directed to control concentration levels in the ash. Our study looked at several processes for the selective removal of chloride and potassium from precipitator ash. We adopted the following methodology: quantification of all mass flow rates, quantification of enrichment ratios, material balance calculations on the recovery cycle, and analysis of the economic and technical viability of these processes. This investigation is part of a more general study concerned with the reduction of global water consumption in bleached kraft pulp mills. The general objective of this project is to identify and implement strategies that might help achieve the “closed mill” concept within the eucalyptus pulp industries.

IMPACT ON OPERATING CONDITIONS

The two main functions of recovery boilers are to recover the inorganic chemicals

used in kraft cooking of wood and to use the energy capacity of the black liquor to generate steam for the mill. Before going to the boiler, the concentrated black liquor or “strong black liquor” is mixed with various make-up chemicals to produce a fuel with 40% to 50% of inorganic materials (on a dry basis), including chloride and potassium, that enter the process mainly as components of wood. The chloride concentration in black liquor is typically 0.1% to 0.8% of the liquor dry solids, and can reach 3% to 5% in closed cycle processes. The content of potassium usually varies between 1% and 3% [1]. When this fuel is burned, these compounds contribute to a lower melting temperature of the “ash” or smelt. Some of these ash particles are dragged with the gas stream and form deposits on tube surfaces in the upper furnace of the recovery boiler. If they are not periodically removed, they can plug the flue gas passages. Excessive deposit accumulation decreases the boiler capacity and causes severe losses of production. The risk of creating a corrosive environment, which may damage tubes, also increases drastically [1].

These deposits are characterized by two distinct melting temperatures: the temperature at which the liquid phase starts to appear and the temperature above which the material is completely liquid (the complete melting point). Between these two points, there are at least two other temperatures that are important: the sticky temperature (T_{sticky}), when the deposit contains between 15%

and 20% liquid phase, and the radical deformation temperature (T_{RD}) when it contains about 70% liquid phase [2]. These values define a region in which the deposit becomes sticky and can cause massive accumulation.

The enrichment of chloride and potassium in the boiler ash lowers the melting point of these deposits. The sticky temperature can decrease by as much as 280°C as chloride content increases from 0% to 10% by mole Cl/(Na+K) [1]. The effect of potassium is similar to chloride, but not as dramatic, particularly when the chloride content is below 1.5% by mole Cl/(Na+K). Thus, to avoid deposit formation and plugging, the Cl and K concentrations in the recovery cycle should be reduced and maintained at minimum values.

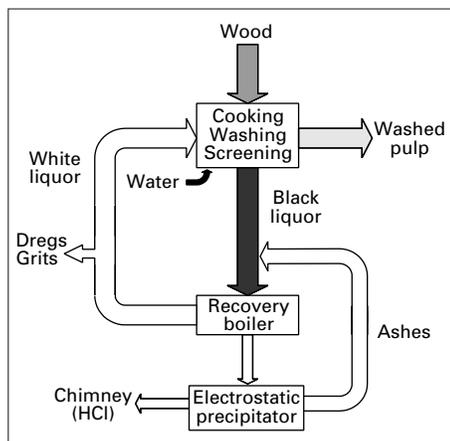
REMOVAL PROCESSES

Some kraft mills simply purge part of the ash collected in the electrostatic precipitator in order to control the concentrations of these NPEs in the recovery cycle. This causes a significant loss of sodium sulfate and sodium carbonate, resulting in additional costs for make-up chemicals [3]. Through a literature survey, we identified several attractive processes for Cl and K removal: leaching, evaporation/crystallization, and ion-exchange. These processes have been used to treat precipitator ash, because it is a stream enriched in chloride and potassium and is easier to deal with than alternatives such as green or white

NONPROCESS ELEMENTS

PROCESS	UTILITIES	% REMOVAL K	% REMOVAL Cl	% RECOVERY NA	% RECOVERY SO ₄
Leaching [5] "Spent-acid" Steam	Fresh water	100	90	70	90
Evaporation/ Crystallization [8]	LP steam Cooling water Makeup water HP steam	90	90	70-80	70-80
Ion-exchange [8]	Fresh water Steam	5	95	> 90	> 90

1. Utilities and performances associated with each process.



1. Unbleached pulp plant and recovery cycle schematic diagram.

liquor, which are highly corrosive.

Moy and colleagues proposed leaching ash to selectively separate sodium chloride (NaCl) from sodium sulfate (Na₂SO₄) [4]. In this process, ash is mixed and leached with a liquor, in which all the NaCl is dissolved, yielding a saturated liquor with the same NaCl/Na₂SO₄ ratio (3:1) as found in the recycling liquor, at a temperature of 65°C, and a pH of 4.5. The resultant slurry is filtered to recover the sodium sulfate and sodium carbonate. This process was implemented on an industrial scale in 1973, but due to corrosion problems and plugging of the piping, it was abandoned in 1976. A modified leach-

ing system was designed by Sandwell Inc. in collaboration with students of the Department of Chemical Engineering at the University of British Columbia in Canada [3]. In this project, we modified the original system to minimize the corrosion problem and to facilitate the filtration of the solids from the leached slurry.

In the evaporation/crystallization process [5], the ash is first dissolved in water to make a near-saturated solution at about 30% dissolved solids, and is then fed to an evaporator-crystallizer operating under vacuum. As water evaporates from the solution, sodium sulfate crystals precipitate and are separated by filtration from the concentrated mother liquor. Part of this liquor is subsequently recirculated back to the evaporator. In this process, the presence of significant amounts of carbonate and/or potassium can reduce the removal and recovery efficiencies. That is the case, for instance, when burkeite (2Na₂SO₄·Na₂CO₃) crystallizes together with the sodium sulfate. This process has been used in the Champion International Corporation's bleach filtrate recycle in Canton, North Carolina, USA. Recently, the Ahlstrom Machinery Corporation successfully tested this process in a pilot plant capable of treating 2000 tons/day of ash [6].

Another way of removing chloride, developed by Eco-Tec [7-8], involves percolating ash dissolved in warm water (40°C-50°C) through a fixed-bed packed with an amphoteric resin containing both anions and cation-exchange groups. This process uses fine particle resins, countercurrent regeneration with water, short columns heights,

high flow rates, and short-cycle times. **Table I** summarizes the performance and utilities used by these processes.

Other processes tested only at laboratory scale include: electrodialysis using bipolar membranes, liquid-liquid extraction with polyethylene glycol, green liquor cooling crystallization, and evaporation of the white liquor [9-11].

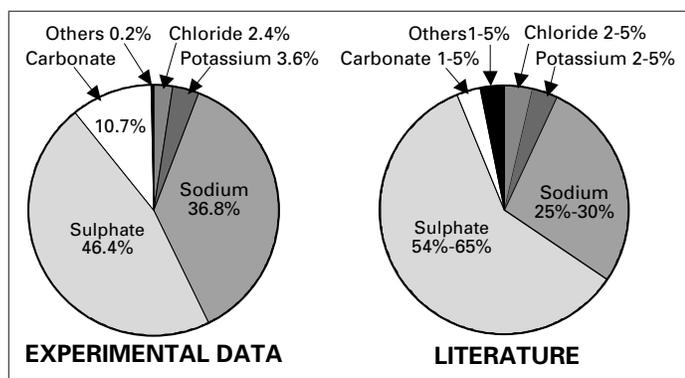
RESULTS AND DISCUSSION

The results obtained in this study are based on information that follows on a more comprehensive project concerned with the reduction of global water consumption using two national pulp mills (mill A and mill B) located in the center and south regions of Portugal, respectively. **Figure 1** gives a schematic representation of the unbleached pulp plant and recovery cycles of these mills.

CHEMICAL COMPOSITION OF ASH

Several samples of ash from the electrostatic precipitators were dissolved in water. We measured their ion concentrations using atomic absorption spectroscopy for sodium and potassium and potentiometric titrations for sulfate, carbonate, and chloride. **Figure 2** shows the chemical composition of ash from mill A. In this figure, the chloride and potassium concentrations are within the typical variation range reported in the literature [12]. However, the samples have higher carbonate and lower sulfate content. This is because the ash composition depends on several variables, such as the composition of the black liquor, the combustion conditions in the lower furnace, the mill's chloride concentration, etc.

The chloride and potassium concentrations [6.1 mole % Cl/(Na+K) and 5.4 mole % K/(Na+K)] have a calculated sticky temperature of 595°C, which is lower than the flue gas temperature (~640°C). When this occurs there is a risk of deposit growth and boiler plugging.



2. Chemical composition of precipitator ash (Mill A).

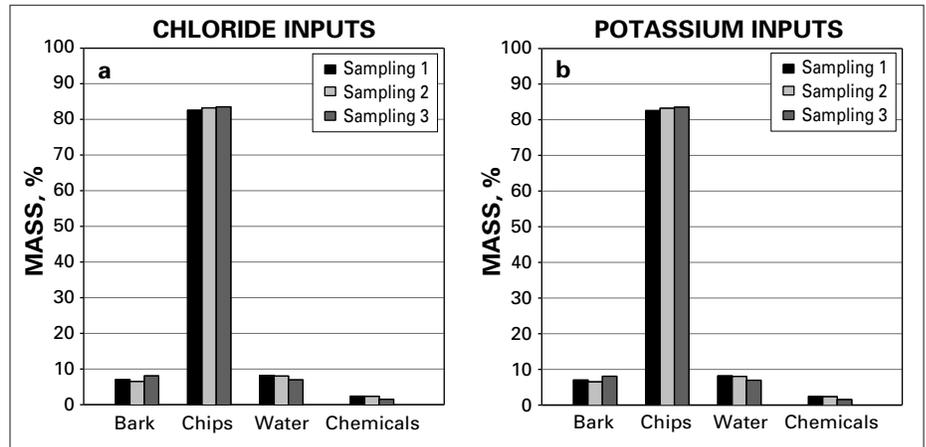
EVALUATION OF INPUTS, OUTPUTS, AND ENRICHMENT FACTORS

Figures 3 and 4 show the chloride and potassium content in the major inputs and outputs of the pulping process. These calculations are based on three sampling plans developed during the 1998 winter-spring-autumn seasons in mill A. As expected, the wood chips are the major input source for Cl and K (80%-85% of the total input). Most of the chloride entering with the wood leaves the system with the bleaching effluents (55%-80% of the total output) and with the white water (15%-18%). The major potassium disposal output streams are the washing effluent (28%-33%), the dregs (7%-29%), and bleaching effluents, together with the white water (55%-49%). In the third sampling, the bleaching wastes exhibit higher percentages of Cl and K than in the others due to changes introduced in the process to reuse part of the washing effluent. This also explains the increasing amount of potassium leaving the process with the dregs.

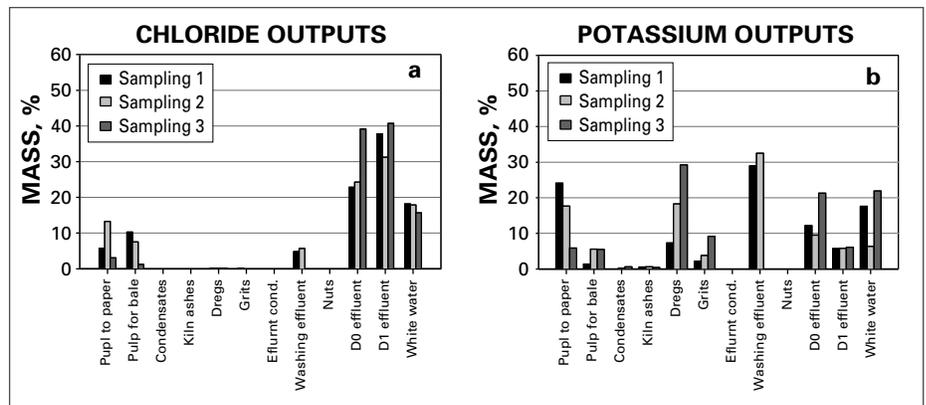
Figures 5a and 5b show average enrichment factors for chloride and potassium in three streams of pulp mills A and B. The enrichment factors (EF) of Cl and K are expressed as mole% of Cl/(Na+K) and K/(Na+K), and are based on the concentration in the as-fired black liquor (BLS). As indicated in Fig. 5, these ratios are greater in the precipitator ash ($EF_{Cl} = 2.35$ and $EF_K = 1.63$) than in the white liquor stream ($EF_{Cl} = 1.21$ and $EF_K = 0.93$). For other pulp mill streams that were not evaluated, such as green liquor, smelt, and weak and strong black liquors, the literature [13] indicates chloride ratios between 0.85 and 1.10. These values are still less than the value 2.35 obtained for the EF of chloride. Thus, the most effective way to remove chloride and potassium in the recovery cycle is to treat the ash stream from the electrostatic precipitator.

EVALUATION OF THE REMOVAL PROCESS AT AN INDUSTRIAL SCALE

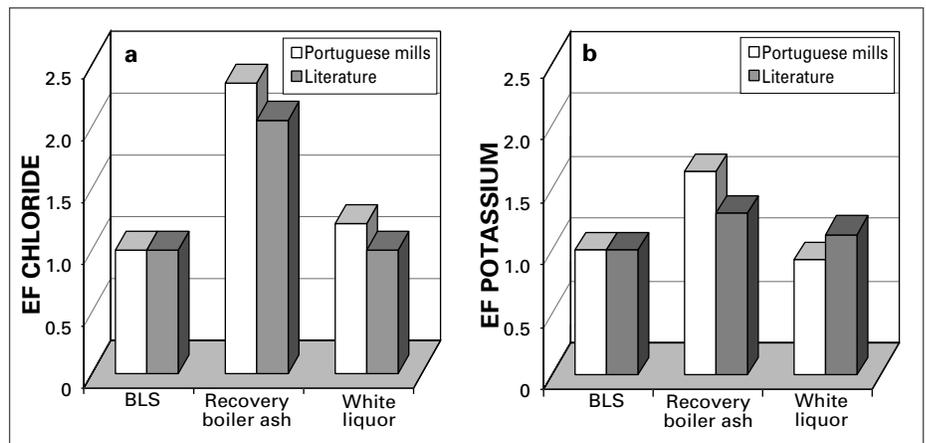
This part of the work was directed at evaluating the relative performance of some of the above mentioned processes for removal of chloride and potassium when integrated into the recovery cycle



3. Chloride and potassium inputs of the pulping process.



4. Chloride and potassium outputs of the pulping process.



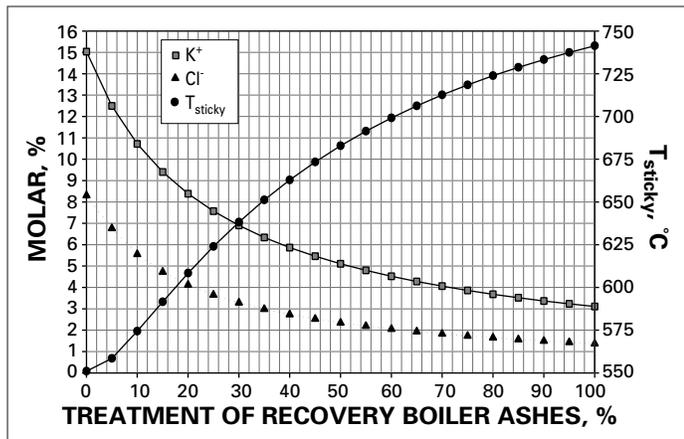
5. Enrichment factors for chloride and potassium.

PROCESS	% REMOVAL Cl	% REMOVAL K	% RECOVERY Na
Leaching	90	100	70
Evaporation/ Crystallization	90	90	76
Ion-exchange	90	5	95

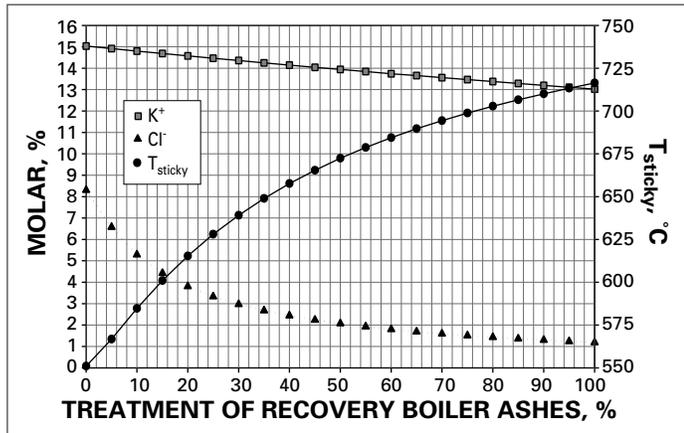
Enrichment factor for Cl = 2.3 Enrichment factor for K = 1.6 Displacement ratio (in relation to the washed unbleached pulp) for Cl and K = 93% Flowrate of ash collected from electrostatic precipitator = 3.7 ton /h.

II. Conditions used for the computer simulations.

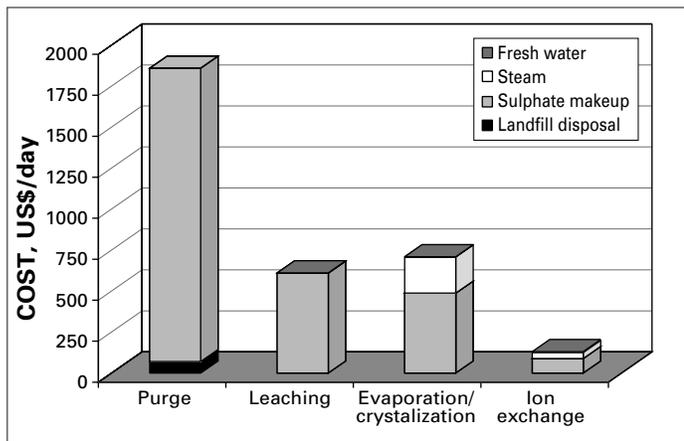
NONPROCESS ELEMENTS



6. Effect of % treatment of ash using the leaching on chloride and potassium concentrations, and sticky temperature.



7. Effect of % treatment of ash using ion-exchange on chloride and potassium concentrations, and sticky temperature.



8. Maintenance costs associated with each technique for removal of chloride and potassium.

of pulp mill B. Computer simulations were carried out using EXCEL/SOLVER software. The calculation methodology was iterative and based on manipulating steady-state concentrations and flow data using a spreadsheet analysis. We determined the Cl and K concentrations of ash captured by the electrostatic pre-

cipitator and recirculated to the black liquor mix tank in order to close the mass balance for each element of the system (Fig. 1). Table II shows the conditions used for the simulations. Figures 6 and 7 show the corresponding results for the leaching and the ion-exchange processes, respectively, where it can be seen how the sticky temperature increased for different levels of ash treatment. As expected, this increase is caused by the reduction of Cl and K levels in the ash. The sticky temperature calculation was obtained by fitting a non-linear regression to the literature data [2].

In evaluating the performance of the processes under study, we adopted the guideline that for a chloride concentration below 1.6 mole% in the BLS, corresponding to 3.7 mole % in the ash stream, with EF=2.35, the effect of Cl and K on thermal properties of the deposits was minimal [12]. In the leaching and evaporation/crystallization, this concentration value is achieved for 25% of the ash treated, corresponding to a 56% reduction in the chloride content of ash. In both cases, the sticky deposit temperature varied from 550°C to 624°C. For the ion-exchange and purge, the same reduction level is achieved with only 22% treatment, with respective increases in the sticky temperature of 550°C to 621°C and 550°C to 623°C. Thus, all processes yield almost the same sticky temperature, even for the ion-exchange method, which is not very selective for potassium removal. This demonstrates that for certain levels of reduction in the chloride concentration, the potassium effect on the sticky temperature is insignificant.

The results allowed us to conclude that to maintain acceptable levels of chloride and potassium in the recovery cycle, the technologies studied require approximately the same amount of ash to be treated. In order to decide which is the most attractive solution for the treatment of ash, we prepared a preliminary economic analysis to evaluate maintenance costs associated with each process. We show these costs in Fig. 8. The results indicate that the purge is the most expensive solution, with costs estimated at US\$ 1800/day, mainly due to the sulfate make-up. The ion-exchange process needs less make-up cost because it is effective at sulfate recovery (>90%). The costs associated with the steam consumption are greater for the evaporation/crystallization process than for the ion-exchange process, which has a sulfate product stream and needs less steam to remove water using the kraft recovery evaporators. The evaporation/crystallization process requires more steam to evaporate water from an ash solution at 30% dissolved solids and to produce sodium sulfate crystals that can be returned to strong black liquor. Another cost for both processes, and leaching, results from their use of fresh water. Overall, the ion-exchange and leaching processes appear to be the least expensive solutions in terms of maintenance costs.

CONCLUSIONS

As kraft pulp mills move toward better closure of their process streams, the accumulation of chloride and potassium in the recovery cycle increases the tendency for recovery boiler tube plugging, giving rise to a decrease in boiler capacity. We evaluated some recent and conventional processes for the selective removal of these two important NPEs. Based on sampling data from two pulp mills, the chemical composition of ash, percentages entering (inputs) and leaving (outputs) the process, and

enrichment factors for Cl and K were quantified. Most of the results obtained are within the ranges reported in the literature.

Computer simulations using EXCEL/SOLVER made it possible to calculate the sticky temperature as a function of the ash amount treated for each process studied. All the processes (purge, leaching, evaporation/crystallization, and ion-exchange) when integrated in the recovery cycle require practically the same ash treatment level.

A preliminary economic analysis indicated that the leaching and the ion-exchange processes are the least expensive alternatives in terms of maintenance costs. **TJ**

ACKNOWLEDGMENTS

We gratefully acknowledge financial support granted by the Portuguese Ministry of Science and Technology under Project PRAXIS 3/3.2/PAPEL/2322/95). The authors also thank RAIZ, Instituto de Investigação da Floresta e do Papel, for its technical and financial support.

LITERATURE CITED

1. Adams, T. N., Frederick, W., Grace, T. et al, "Kraft Recovery Boilers," Terry N. Adams, Ed., TAPPI PRESS, Atlanta, Georgia, USA (1997).
2. Tran, H. N., *Tappi J.*, 69(11): 102(1986).
3. Blackwell, B. and Hitzroth, A., "Recycle of bleach plant extraction stage effluent to the kraft liquor cycle: a theoretical analysis," *International Chemical Recovery Conference Proceedings*, TAPPI PRESS, Atlanta (1992).
4. Moy, W. A., Joyce, P., and Styran, G. E., *Pulp Paper Mag. Can.*, 75(4): 88(1974).
5. Shenassa, R., Douglas, W., Dick, P., and Costa, M., "Chloride and potassium control in closed kraft mill liquor cycles," *Pulp Paper Can.*, 97(5), T173-179 (1996).
6. Koskineniemi, J., Vakkilainen, E. Paju, R. and Hanninen, E., *Appita J.*, 52(6): 460(1999).
7. Minday, A. M., Reid, D. W., and Brown, C. J., "An overview of various strategies for balancing salt cake, chloride and potassium levels in an ECF kraft mill," *Proceedings of the 1997 Minimum Effluent Mills Symposium*, TAPPI PRESS, Atlanta, 1997, p. 115.
8. Brown, C. J., Sheedy, M., Paleologou, M., and Thompson, R., *Pulp Paper Can.*, 100(8): T251(1999).
9. Thompson, R., Paleologou, M., and Berry, R. M., *TAPPI J.*, 80(6): 154(1997).
10. Henricson, K., Kiiskila, E., and Virkola, NE, *Paperi Puu*, 57(10): 643(1975).
11. Pryke, D.C., Reeve, D.W., Lukes, J.A., et al., *Pulp Paper Can.*, 84(2): 59(1983).
12. Earl, P.F., Dick, P.D., and Patel, J.-C., "Removal of chloride and potassium from the kraft recovery cycle," presented at the 1995 Canadian Pulp and Paper Association Pacific Coast and Western Branches Technical Conference.
13. Tran, H. N., Barham, D., and Reeve, D. W., *Pulp Paper Can.*, 91(5): T185(1990).

Received: January 25, 2002
 Revised: September 12, 2002
 Accepted: September 16, 2002

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the April *Solutions! for People, Processes and Paper* magazine (Vol. 86 No. 4)

INSIGHTS FROM THE AUTHORS

This study was part of a research project to evaluate strategies to reduce water consumption in Portuguese pulp mills. To reduce water use requires mills to implement significant changes in their effluent management systems, with implications in the process and technologies used at present. Accumulation of nonprocess elements (NPEs), namely chloride (Cl) and potassium (K), is the major concern when such changes are made in the bleach plant, leading to an increase in water reuse. Otherwise, high concentration levels of chloride and potassium cause serious problems in the recovery boiler operation.

Our study involved experimental work to characterize the major streams of the pulping process and computational simulations using the EXCEL/SOLVER for a preliminary technical and economical evaluation of various alternatives to treat boiler ash in order to remove chloride and potassium. The most difficult aspect of the research was obtaining consis-

tent experimental data to be used in the mass balance equations solved iteratively by computer.

The next step is to carry out studies on the ion-exchange process in terms of experimental evaluation of equilibrium and kinetics parameters using a suitable resin for removing chloride. This process is one of the more attractive alternatives for ash treatment, as indicated by our study.

Ferreira, Soares, Egas, and Castro are with the Department of Chemical Engineering, University of Coimbra, Pólo II, Pinhal de Marrocos, 3030-290 Coimbra, Portugal. Email Ferreira at eq1lmf@eq.uc.pt.



Ferreira



Soares



Egas



Castro