

# EVALUATION OF SOURCES AND ROUTES OF NON-PROCESS ELEMENTS IN A MODERN EUCALYPTUS KRAFT PULP MILL

Authors\*: Javier Doldán<sup>1</sup>  
 Outi Poukka<sup>2</sup>  
 Keijo Salmenoja<sup>2</sup>  
 Marcos Battegazzore<sup>3</sup>  
 Virginia Fernandez<sup>3</sup>  
 Inés Eluén<sup>3</sup>

**Keywords:** Enrichment, kidneys, modern eucalyptus kraft pulp mill, non-process elements

## SUMMARY

Modern pulp mills tend to apply cleaner and environment friendly processes generally by recycling and reusing various streams into the evaporation system and the reduction of discharges. This kind of closure leads to a build-up of non-process elements (NPEs) mainly in the chemical recovery system. Chemicals which accumulate in the mill cycles originate either from the wood raw material, process water and make-up chemicals. Natural purging places, generally referred as kidneys, are associated to the removal of these elements as green liquor dregs, grits or lime mud. The purpose of this study is to evaluate the routes of NPEs in a modern eucalyptus kraft pulp mill. An extensive sampling campaign was carried out at the studied mill. Samples were taken from all the main process streams to achieve an overall picture of the inputs, outputs, and enrichment in the mill. Complete mass balances were accordingly constructed for the entire mill. The results of this study can be utilized in the non-process element management at the mill and they serve as a good basic material for the further mill specific simulations.

## INTRODUCTION

Non-process elements (NPEs) are defined as chemical elements that are present in the process cycles and do not participate in the pulping process [2]. Carbon (C), hydrogen (H) and oxygen (O) form the organic material, and are not regarded as NPEs [1]. NPE concentrations increase by the reduction of effluent flows from kraft pulping and by the closure of the chemical cycles. Non-process elements can be classified into three general types [1]:

- those that are highly soluble in alkali and can build up without limit (K and Cl<sup>-</sup>);
- those that are partially soluble in alkali and can build up to significant levels before being naturally purged by precipitation (Al, Si, P);

- those that are highly insoluble in alkali and are removed with green liquor dregs and, therefore, do not build up (Ca, Mg, Ba, Fe).

With another point of view by ULMGREN [14] is that NPEs can be divided in two main groups:

- those that are purged with green liquor dregs (Mg, Ca, Mn, Fe and Cu);
- those that are accumulated in the liquor cycle and form soluble ions in alkaline solutions (Al(OH)<sup>4-</sup>, SiO<sub>2</sub>(OH)<sub>2</sub><sup>2-</sup>, Cl<sup>-</sup> and K<sup>+</sup>).

NPEs can enter the cycle with the wood; make-up chemicals and make-up lime [3, 4, 14]; with process water; with the bleaching chemicals; and with recycled effluent streams and biosludge [1]. The major part of the NPE intake is via wood chips, where the content of Mg, Ca, K and Cl<sup>-</sup> can be rather high, while other elements, e.g. transition elements, are present only on trace levels [5, 14]. Pulpwood raw materials differ in the amount of NPEs depending on the location (ground composition), species and age. Tree mineral element absorption depends on different factors like: specie, genetics, clone, growth rate, high or low soil availability of elements ions, water accessibility, etc. For instance, *Eucalyptus* species like *E. dunnii* and *E. globulus* seem to absorb more NPEs than *E. grandis* per ton of produced biomass [6]. FREDDO [7] presented another example of NPE content in *Eucalyptus* species, where K and Ca were the most common elements present in this hardwood species. FERREIRA *et al.* [8] stated that wood chips are the major input source for Cl<sup>-</sup> and K being the 80% to 85% of the total input in a Portuguese eucalyptus mill. Other sources are the make-up chemicals used to replace chemical losses in the process, and biosludge when burnt in the recovery boiler.

Accumulation of NPEs in the pulping process may cause scaling problems on recovery boiler heating surfaces and screens, it may also induce increased use of bleaching chemicals during later stages, and may disturb clarification and filtration [9, 10, 14]. In the recovery process, NPEs are enriched in different places and streams. This accumulation is generating problems such as scales, deposits, plugging and corrosion of several equipments [1, 14]. Accumulation of Cl<sup>-</sup>, K and Mg may promote corrosion and plugging of the gas passage in the

## Authors' references:

1. Silvicultural Projects Department - LATU - Av. Italia 6201, C.P. 11500 Montevideo, Uruguay,
2. Oy Metsä-Botnia Ab, Finland
3. UPM Fray Bentos mill – Ruta Puente Puerto Km 307 Fray Bentos, Uruguay

Corresponding author: Javier Doldán – E-mail: jdoldan@latu.org.uy

recovery boiler [8, 11, 14]. Ca, Ba, Al and Si may generate scales on heat transfer surfaces in the digester and evaporation plant. P, Mg, Al and Si may cause difficulties in settling and filtration processes at recausticizing and may produce lime inerts in lime cycle [9, 12].

Due to the rapid enrichment of NPEs into the chemical cycles in a modern eucalyptus kraft pulp mill, natural (kidneys) and artificial purges must both be applied. Some water soluble NPEs can be purged with effluent streams. For other non-soluble NPE, filtration or screening processes are natural kidneys. Main kidneys are associated to the removal of these elements as green liquor dregs, grits, lime mud or recovery boiler and lime kiln electrostatic precipitator (ESP) dust.

Potassium and chloride have high solubility and therefore do not have natural kidneys in the pulp mill. Thus, K and Cl<sup>-</sup> have to be removed by dedicated equipment [9]. Unless K and Cl<sup>-</sup> are water soluble, they are rapidly enriched in tightly closed eucalyptus mills. Some kraft pulp mills simply purge part of the ash collected in the recovery boiler ESP in order to control the concentrations of the NPEs in the recovery cycle. This causes a significant loss of sodium, resulting in additional costs for make-up chemicals. In general, these processes are conducted in order to reduce the chloride and potassium concentration before mixing with heavy black liquor [8]. In existing removal processes, K and Cl<sup>-</sup> are removed with high efficiency and simultaneously minimizing sodium and sulphur losses.

The objective of this study was to evaluate the routes of Na, S, Cl<sup>-</sup>, K, Ca, Mn, Mg, Al, Si and P in a modern eucalyptus kraft pulp mill. On the basis of an extensive sampling campaign, the main process streams were studied to achieve an overall picture of the inputs, outputs, and enrichment in the mill. A complete mass balances were accordingly constructed for the entire mill.

The results of this study can be utilized in the non-process element management at the mill and they serve as a good basic material for the further mill specific simulations.

MATERIALS AND METHODS

Sampling and sample preparation

An extensive sampling campaign was carried out at Botnia's Fray Bentos mill, Uruguay (UPM mill since 2010) on February 2009. Samples were taken from all the main process streams to achieve an overall picture of the inputs, outputs, and enrichment of non-process elements in the mill. Around 70 samples were taken from 35 different sampling points, repeating the procedure in two different days, see Figure 1. Process conditions during the samplings were stable and representative for normal mill operation at that time.

Analysis methods

COD analyses were performed by ISO 15705 (modified) for filtrates, carry-overs and waste waters. Wet digestion or acid dissolution followed by ICP (Inductively Coupled Plasma) was used for the determination of metals in different streams by a Botnia's own method. Matrix modification in the metal analyses by ICP instrument was needed to reduce the interference of the major component of the sample in order to measure the elements present in trace level. In matrix modifications the content of standard solution is matched to the samples. Chloride (Cl<sup>-</sup>) was determined by SCAN-N 4:78 for white and green liquors and by ISO 9197 for pulp samples. SO<sub>4</sub><sup>2-</sup>, oxalate and ESP dust Cl<sup>-</sup> analyses were performed with Ion Chromatography

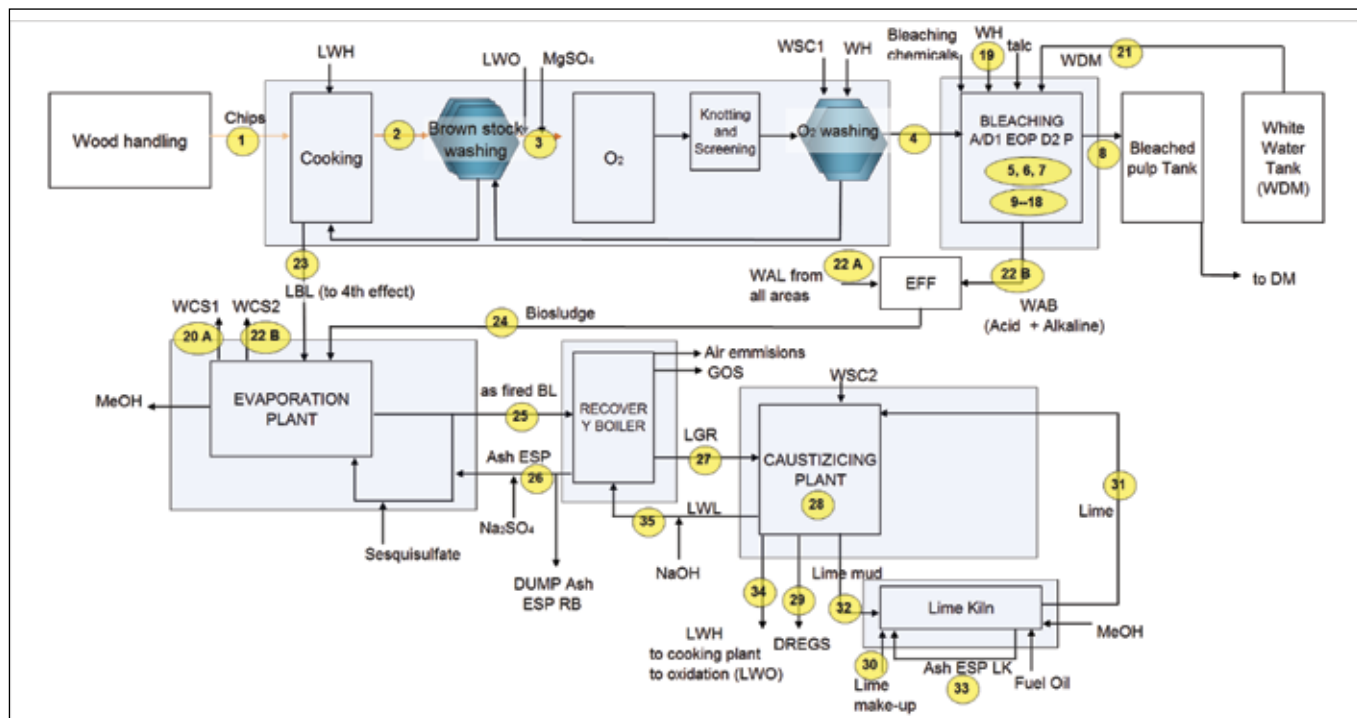


Figure 1. Sampling points and mill processes diagram

(IC) by a Botnia's own method.  $\text{OH}^-$ ,  $\text{HS}^-$  and  $\text{CO}_3^{2-}$  on white and green liquor were determined under SCAN-N 30. On weak black liquor and black liquor as fired,  $\text{OH}^-$  was analyzed by SCAN-N 33:94,  $\text{HS}^-$  by Ag-titration, SCAN-N 31:94 and  $\text{CO}_3^{2-}$  by SCAN-N 32. Lime make-up, lime mud and lime free CaO was determined by SCAN-N 25.

Uncertainties of NPE results of different samples (white liquor, weak black liquor, ESP ash and lime mud) can be estimated as 15%.

### Process data and construction of non-process element balances

Process information from the different departments of the mill was gathered during the sampling days. Important flows and pulp concentrations were obtained from mill measurements and mill data system. The purpose of making balances is to describe the routes of NPEs in the process circulation. For that reason, element balances were made for the main mill departments: cooking and oxygen delignification, bleaching plant, evaporation plant, recovery boiler, causticizing plant + lime cycle. Balances were constructed utilizing analysis data and process data from the mill data system. The balances were calculated for the production level of 3400 adt/d bleached pulp. Sodium and sulphur were used as references to close the balances and all the NPE values were calculated according to resultant flows.

## RESULTS AND DISCUSSION

### Na and S balance

The majority of sodium entering into the fiberline comes with the white liquor to the cooking, ca. 311 kg/adt and to the oxygen delignification, about 25 kg/adt. Almost all the sodium entering with the bleaching chemicals is directed to the effluents. The majority of sodium in the fiberline goes to the evaporation plant in weak black liquor. Sodium is passing through evaporation, recovery boiler and causticizing almost without changes. The outputs from the chemi-

cal cycle are placed in the purged ESP ash, the brown pulp to the bleach plant and dregs + lime mud pre-coat filter. The ESP ash must be purged due to the high chlorine concentration of the black liquor. These losses are generally recovered by addition of neutralized sesquisulfate into the heavy black liquor, and sodium hydroxide (NaOH) to the white liquor tank.

The balance of sulphur in the mill is a very well controlled issue. Sulphur is following mainly the liquor cycle and is not detected in the lime cycle. It is incoming to the fiberline through the white liquor and the oxidized white liquor. Other inputs are the magnesium sulphate ( $\text{MgSO}_4$ ) to the  $\text{O}_2$  delignification, bleaching chemicals (sulphuric acid for pH adjustment), and white water from the drying machine (from recirculation and addition of pH adjustment chemicals). No significant amount of sulphur was observed in the bleached pulp. In the same way as sodium, sulphur additions as neutralized sesquisulfate are stabilizing the general S balance in the chemical recovery system. Outputs from the system are occurring mainly via the purged recovery boiler ESP ash. A detailed Na/S balance is shown in Figure 2.

### NPE sources, outputs and accumulation

The studied balances are demonstrating that wood is the main source of NPEs into a modern eucalyptus pulp mill. This kind of result has already been obtained for other pulp mills [5, 14]. In this mill, the chips source is a mixture of different eucalyptus sub-species and the mill is particularly careful with the management of sub-species ratio. Still, the variety of wood sources incoming to the mill - for example, concerning ground composition at plantations -, can make it extremely difficult to ensure a relatively stabilized flow of NPEs. In this case, K, Cl<sup>-</sup> and Ca are the more concentrated NPEs in the utilized wood, see Table 1. Potassium and chloride are showing values within the expected ranges [6]. On the other hand, calcium is introduced into the mill at higher amounts than expected. This is corroborating the high Ca content of *Eucalyptus grandis* from Uruguay [13].

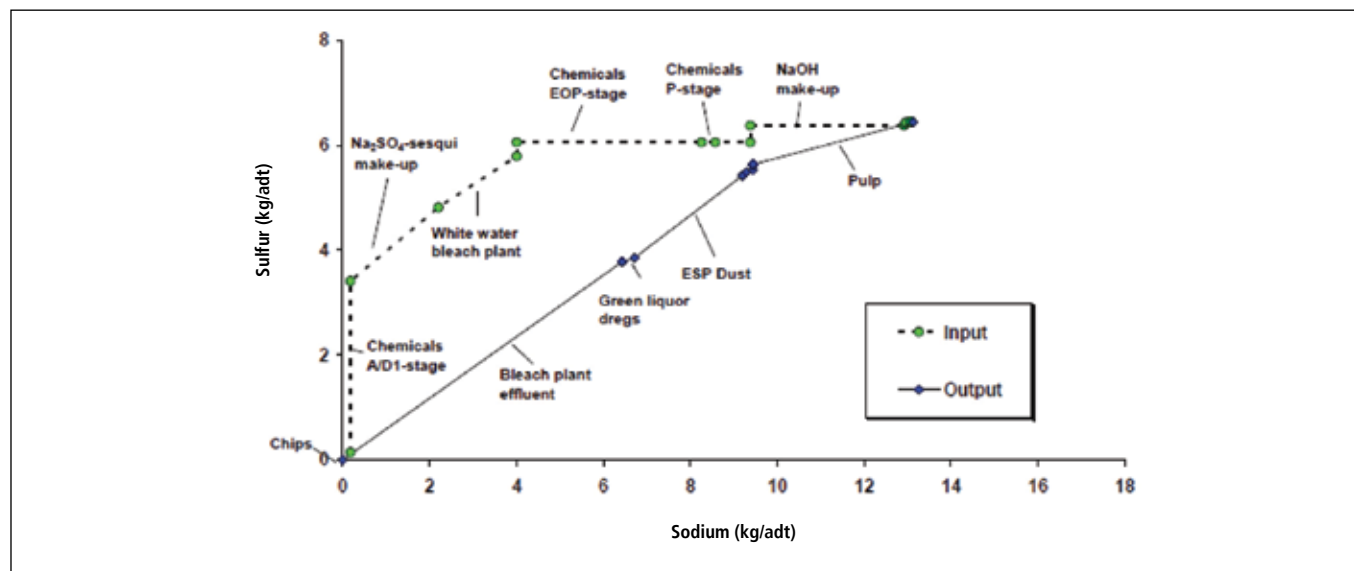


Figure 2. Na/S balance for the entire mill

**Table 1. Non-process elements most important sources and outputs quantification (g/adt)**

Sample point	Ca	K	Cl <sup>-</sup>	Mn	Mg	P	Al	Si
Chips <sup>(S)</sup>	2193	914	420	62	256	121	12	24
Biosludge <sup>(S)</sup>	143	17	16	14	89	41	42	197
Unbleached pulp <sup>(O)</sup>	1440	405	13	14	207	31	14	90
Purged ESP ash <sup>(O)</sup>	1	466	342	0.1	0.4	0.2	0.1	0.9
Returned ESP ash <sup>(R)</sup>	12	5427	3979	2	4	2	0.8	11
Lime mud from lime filter <sup>(R)</sup>	-	58	0	130	2100	5600	170	1000
Pre-coat filter (green liquor dregs + lime mud) <sup>(O)</sup>	2049	12	2	30	209	40	35	81

<sup>(S)</sup> Source; <sup>(O)</sup> Out-put; <sup>(R)</sup> Recycle

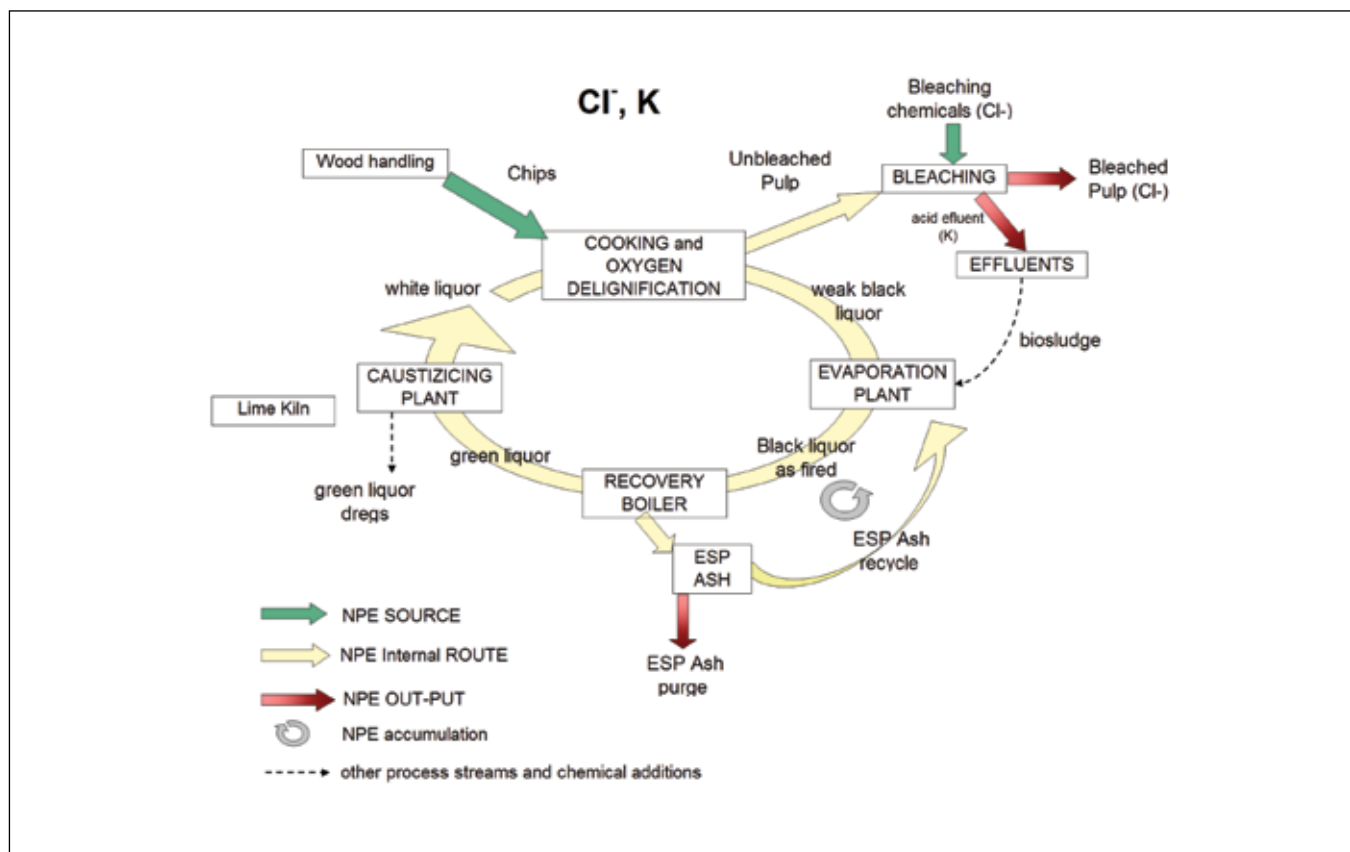
The amount of Ca incoming with the wood chips is higher than the circulated in the black liquor and white liquor. There is no evident enrichment of Ca in the liquor cycle and a great amount of it is passing through with the brown stock to the bleaching plant. Anyway, the calcium concentrations inside brownstock represent a high risk of scaling on washing, knotting and screening equipments. Acidic stages (A/D1) are dissolving almost all of the Ca compounds, which are, therefore, discharged with the acidic effluent.

It was confirmed that at Fray Bentos modern and well-closed mill chloride and potassium remain in the circulation and, thus, are enriched in the black liquor cycle (see Figure 3).

The only effective output place for K and Cl<sup>-</sup> is the ESP ash from the

recovery boiler. However, purging of precipitator ash could not keep the K and Cl<sup>-</sup> concentrations on a desired level. Purging of ESP ash resulted in high Na and S losses (2 kg Na/adt and 1.3 kg S/adt) and had to be recovered as make-up chemicals resulting in increased costs.

Due to the high level of chloride and potassium detected in ESP ash after 6 months of operation, the mill had already decided to install an ash leaching process by the time this sampling campaign was done. The study confirmed the need of the system. Before the start-up of the leaching system, reported potassium and chloride levels in the recovery boiler ESP ash were 8.2% and 5%, respectively. Three months later, the level of K and Cl<sup>-</sup> had decreased to about 3% and 1.4%, respectively (Figure 4).



**Figure 3. Chloride and potassium sources, routes and outputs general diagram**

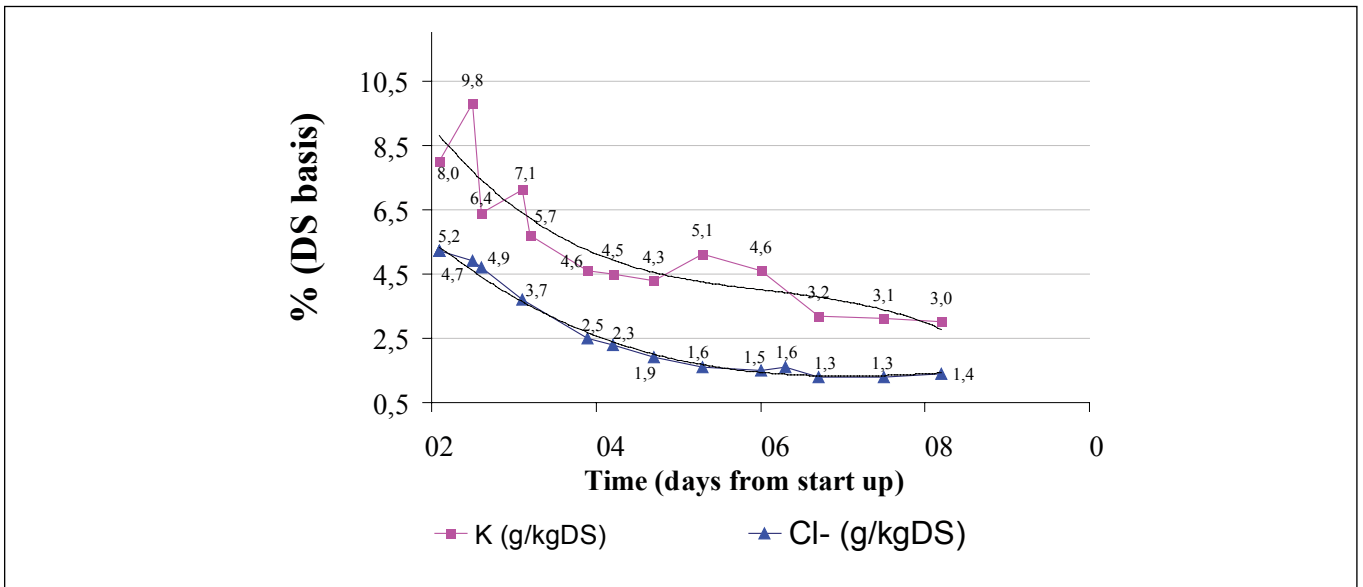


Figure 4. Chloride and potassium levels in the recovery boiler ESP ash from the start-up of the ash leaching system. Modified from the mill data information

The results obtained in this work show that P, Mg, Si and Al are enriched in the lime cycle (see Figure 5 and Table 1). An augmented content of these NPEs considerably increases the dead load of the lime kiln and thus may produce a negative impact on the energy consumption.

Phosphorous was accumulated in great amounts in the lime mud and it may produce poor quality lime and operational problems [1]. Therefore, P is the major dead load component in the lime cycle. The only output routes of P from the lime cycle are the lime mud pre-coat filter for dregs and ESP ashes from the lime kiln. Phosphorous can

also be controlled by purging the lime mud.

Magnesium, silicon and aluminium are also accumulated into the lime cycle. Levels of Mg, Si, and Al were 2300 g/adt, 1000 g/adt and 180 g/adt, respectively. Manganese is present in the lime mud in a higher level than the amount observed in the liquor cycle. However, this element does not pose any significant problems in the recovery area.

Biosludge added into the black liquor in the evaporation plant has relatively high levels of Al, Si, and P, representing the main route into the liquor cycle for these elements. Aluminium concentration in the

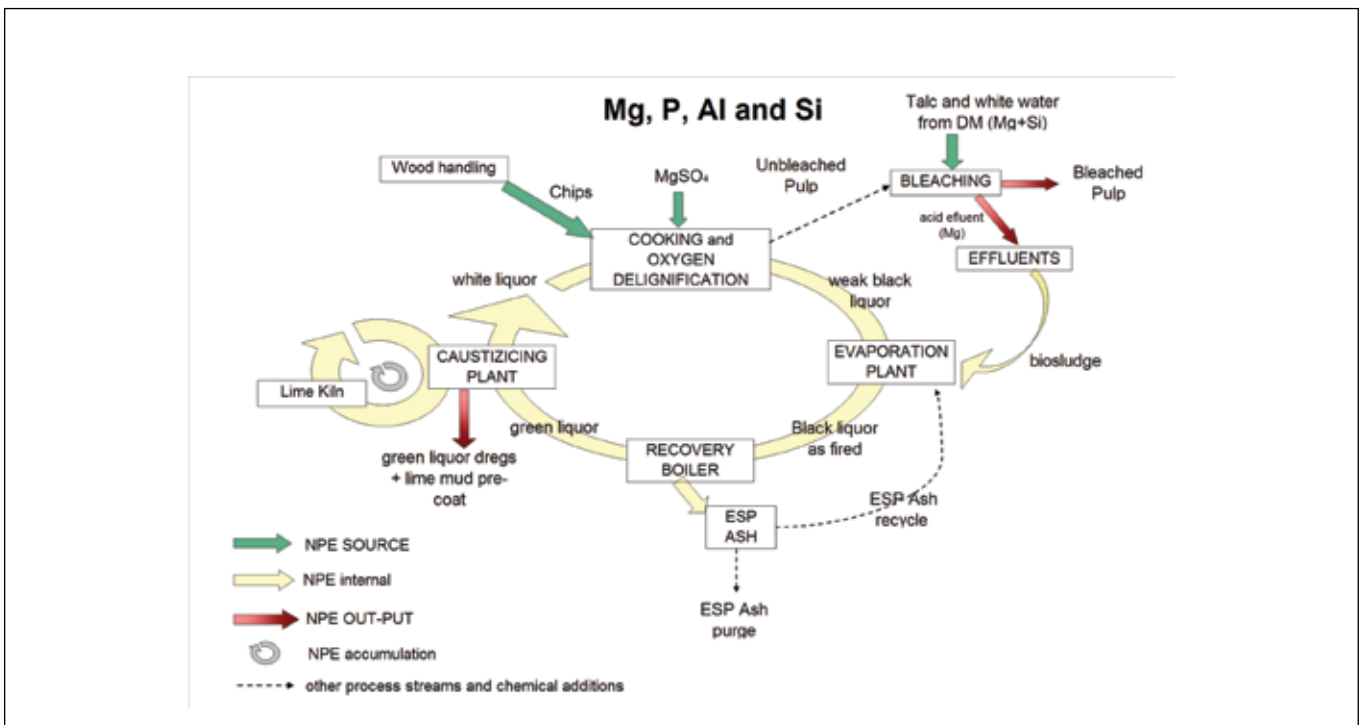


Figure 5. Magnesium, phosphorous, aluminium and silica sources, routes and outputs general diagram

lime cycle was not significant because of efficient removal of dregs in green liquor filtration.

One way to take out Al is the addition of  $MgSO_4$  to the smelt dissolving tank. Magnesium ions are precipitated as solid magnesium hydroxide in an alkaline solution, but in the presence of aluminate ions, hydrotalcite ( $Mg_6Al_2(CO_3)(OH)_{16} \cdot 4(H_2O)$ ) is formed instead. Thus, the possibility to purge aluminate ions as hydrotalcite with the green liquor dregs is favoured by decreasing the weak white liquor  $OH^-$  concentration, by lowering the temperature, by decreasing the concentrations of  $HS^-$  and Si and by increasing the concentration of  $CO_3^{2-}$  [14].

## CONCLUSIONS

Non-process elements sources, routes and outputs were studied at a eucalyptus kraft pulp mill. Information collected from the extensive sampling campaign in the whole mill, process data and analyses were processed. This information enabled to construct complete balances for each of the studied non-process element. This basic data can be utilized in new mill processes designing and implementation.

It was confirmed that wood is the main source of non-process elements in the studied eucalyptus pulp mill. In this case, the mixture of used Eucalyptus wood was rich at K, Cl<sup>-</sup> and Ca. Potassium and chloride are showing values inside the expected ranges.

Very little of the Ca incoming with the wood chips ends up in the black liquor. In the fiberline, Ca is passing through with the brown stock to the bleaching plant. Acid (A/D1) stages are dissolving almost all the Ca compounds that are discharged with the acidic effluent. Since the pulp production is very large, even a small fraction of total Ca ions precipitating as  $CaCO_3$  can result in severe scaling problems at brown stock washing, knotting and screening equipments.

Corrosion was detected in the recovery boiler superheaters and it was reported to be due to the high concentration levels of chloride and potassium in the as-fired black liquor. The only effective output for these elements is the recovery boiler ESP ash. The ash leaching process started in Fray Bentos mill after the sampling campaign, has dramatically decreased the K and Cl<sup>-</sup> levels in as-fired black liquor.

Biosludge recycled into liquor cycle seems to be the main input of aluminium, silicon and phosphorous. Aluminium is not highly accumulated in the lime cycle because of an efficient green liquor dregs removal. Non-process elements enriched at the lime cycle were Mg, Al, Si and Mn. All these NPEs are increasing the dead load in the lime kiln. With the present mill configuration, the usual output for these elements is the lime mud used in the dregs pre-coat filter. ESP ashes from the lime kiln could be considered as an alternative purging spot for phosphorous. ■

This paper has been presented at the XXI TECNICELPA Conference and Exhibition / VI Iberoamerican Congress on Pulp and Paper Research - CIADICYP 2010

## REFERENCES

- Tran, H. and Vakkilainen, E. K. (2007). *Advances in the Kraft chemical recovery process*. Research program on Increasing Energy and Chemical Recovery Efficiency in the Kraft Process, NSERC and a consortium of companies.
- Nurmesniemi, H., Pöykkiö, R., Perämäki, P. and Kuokkanen, T. (2005). *The use of a sequential leaching procedure for heavy metal fractionation in green liquor dregs from a causticizing process at a pulp mill*. *Chemosphere* (61): 1475 - 1484.
- Rocha, T., Duarte, A., Duarte, R., Neto, C. P., Sampaio, R., Oliveira, J. and Caldeira M. T. (1998). *Analysis of NPE of the main process streams of an Eucalyptus bleached kraft pulp mill: preliminary results*. Proc. Fifth European workshop on lignocellulosic and pulp. *Advances in lignocellulosics chemistry for ecologically friendly pulping and bleaching technologies*. University of Aveiro, Portugal. pp. 345 - 348.
- Taylor, K. and McGuffie, B. (2006). *Investigation of non-process elements chemistry at Elk Falls mill - green liquor clarifier and lime cycle*. PAPTAC, Parksville Conference.
- Lundkvist, F., Brelid, H., Saltberg, A., Gellerstedt, G. and Tomani, P. (2006). *Removal of NPE from hardwood chips prior to kraft cooking*. *Appita*, 59 (6): 493 - 499.
- Foelkel, C. (2005). *Minerais e nutrientes das árvores dos eucaliptos* www.eucalyptus.com.br Eucalyptus Online Book & Newsletter. November.
- Freddo, A. (1997). *Elementos minerais em madeiras de eucaliptos de Acacia Negra e sua influencia na industria de celulose kraft branqueada*. Universidade Federal de Santa Maria, Santa Maria (RS), Brasil.
- Ferreira, L.M., Soares, M., Egas, A. P. and Castro, J. A. (2003). *Selective removal of chloride and potassium in kraft pulp Mills*. *Tappi Journal*, 2(4): 21-25.
- Rabelo, M. S., Morgado, A. F. and Mangolini Neves, J. (2001). *The influence of enhancement of Non-process elements (NPEs) on a totally chlorine free (TCF) bleaching plant with filtrates mill closure system*. 7th Brazilian Symposium on the chemistry of lignins and other wood components, poster presentation. Belo Horizonte, MG, Brazil.
- Salmenoja, K., Poukka, O. and Battagazorre, M. (2009). *Management of non-process elements in Eucalyptus kraft pulps mills*. ABTCP.
- Backman, R., Skrifvars, B-J, Hupa, M., Siiskonen, P. and Mäntyniemi, J. (1995). *Flue gas chemistry in recovery boilers with high levels of chlorine and potassium*. Proc. International Chemical Recovery Conference, Toronto, CPPA, pp. A95 - A103.
- Vakkilainen, E. K. (2005). *Kraft recovery boilers - Principles and practice*. The Finnish Recovery Boiler Committée, Valopaino Oy, Helsinki, Finland ISBN 952-91-8603-7.
- Saarela, K.-E. Harju, L., Lill, J.-O., Rajander, J., Lindroos, A. and Heselius, S.-J. (2002). *Thick-target PIXE analysis of trace elements in wood incoming to a pup mill*. *Holzforchung* 56, pp. 380 - 387.
- Ulmgren, P. (1987). *The removal of aluminium from the recovery system of a closed kraft pulp mill*. *Nordic Pulp and Research Journal* 1: 4-9.