Chloride and potassium removal efficiency of an ash leaching system

By C. Gonçalves, H. Tran, S. Braz, F. Puig and R. Shenassa

Abstract: Results of an analysis of the operating data of an ash leaching system show that the system removed 90% of the chloride (Cl) and 82% of the potassium (K) introduced to the system with the precipitator ash. The Cl concentration in the ash was significantly lower, compared to that before the ash system installation, while the K concentration remained at about the same level as before, when the mill was purging ash. The dramatic decrease in Cl concentration and the insignificant change in K concentration in the precipitator ash are likely due to the ash leaching system installation and the high sulphidity operation of the mill.

Chloride (Cl) and potassium (K) are known to have a negative impact on the operation of the kraft chemical recovery process. These elements, despite their small quantities in black liquor, can drastically lower the melting temperature of fly ash deposits, and contribute to severe fouling and corrosion of heat transfer tubes in recovery boilers [1,2].

As pulp mills have tightened their liquor cycle in recent years in order to improve spill control and decrease chemical losses, Cl and K concentrations in the mill liquor have increased, causing problems in recovery boiler operation. This has led to a renewed interest in chloride and potassium removal.

Due to their highly volatile nature at high temperatures, NaCl and KCl vaporize from the recovery boiler char bed, and from in-flight burning black liquor particles. As the flue gas temperature decreases in the back side the boiler, these compounds condense as fume and become enriched in the precipitator ash. The enrichment factors of these species in the ash are typically about 2.5 for Cl and 1.5 for K. As a result, efforts to remove Cl and K from the recovery cycle have been directed at the precipitator ash.

Besides purging precipitator ash periodically, several ash treatment processes are presently available for selectively removing Cl and K from the recovery cycle, using distinctly different principles: leaching, evaporation-crystallization, freezing-crystallization and ion exchange [3]. While the first three ash treatment processes use different principles, they all follow a basic scheme, as shown in Fig. 1. Ash and water are fed into an ash treatment unit where they are mixed and treated. The resulting slurry consists of two parts, liquid and solid. The liquid part, which is essentially the saturated solution of the ash, contains much more Cl and K and much less SO_4 and CO_3 than the solid part. These two parts are subsequently separated in a separation unit. The liquid stream is purged to remove Cl and K, while the solid stream is returned to the mill liquor to recover Na and S.

The efficiency of Cl and K removal of an ash treatment process depends on three main factors: i) the ash concentration in the slurry (or ash/water ratio); ii) the solubility of the individual salts in the slurry; and iii) the degree of solid-liquid separation of the slurry.

The solubility of salt components is governed by the thermodynamics of the system, i.e. concentration, composition and temperature, which have been intensively studied.



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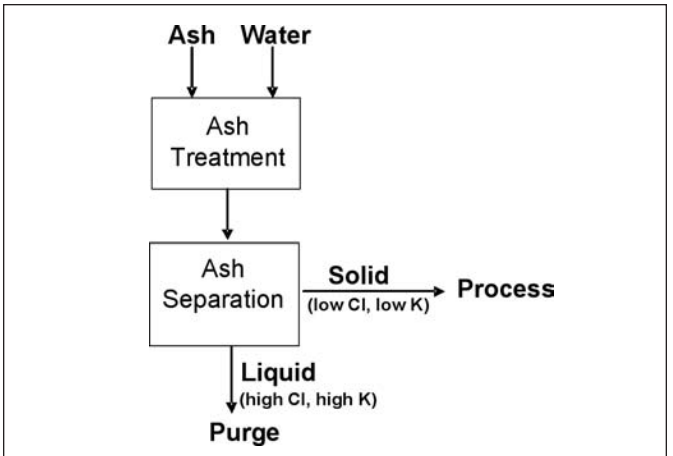


FIG. 1. Basic Cl and K ash treatment scheme.

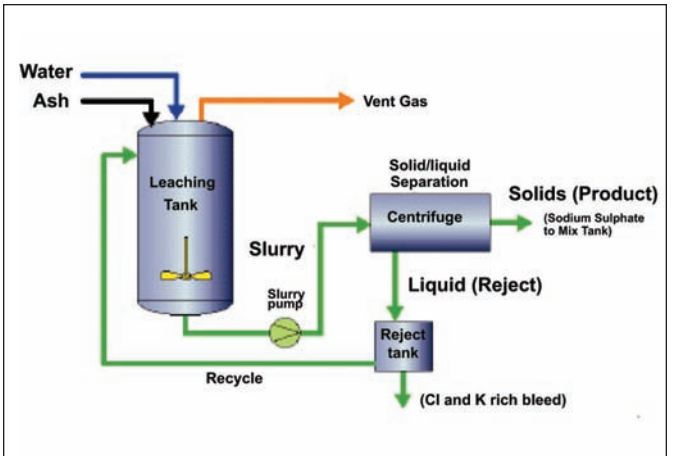


FIG. 2. Ash Leaching System at Aracruz [2].

The degree of solid-liquid separation depends on equipment design, and capacity and the separation method employed in the process. It also depends greatly on the physical and morphological properties of the solids (or crystals). If the degree of separation of a process is 0%, there will be no separation and hence no Cl and K removal. If the degree of separation is 100%, the liquid will be completely separated from the solids, or the solids will be "dry" and contain no liquid. In practice, it is impossible to achieve complete separation; the solids are always "wet" (contain some liquid), which lowers the Cl and K removal efficiency of the treatment system.

Understanding the degree of liquid-solid separation of an ash treatment system, and the main parameters that influence the degree of separation, is critically important for maximizing the Cl and K removal efficiency of the system. This work consists of two parts:

Part 1 involves an analysis of the operating data of the ash leaching system at Aracruz Celulose S.A., Aracruz, Brazil, to determine the Cl and K removal efficiency of the leaching system, and to examine how the removal process affects the overall Cl and K concentrations in the mill liquor cycle.

Part 2 involves a series of laboratory experiments performed on precipitator ash samples collected from different recovery boilers, to examine the properties of ash slurry and how they may affect the degree of liquid-solid separation.

This paper discusses only the results of Part 1 of the study.

Ash leaching system at aracruz

System Description

The ash leaching system at the Aracruz mill is a Metso Power unit installed in May 2002. It was designed to process about 60 t/d of precipitator ash from Boiler A, which is one of the three recovery boilers at Aracruz. The system consists of three main components: a leaching tank, a centrifuge and a reject tank, Fig. 2.

Precipitator ash from Boiler A is mixed with hot water to form slurry in the leaching tank. The ash-to-water ratio and the temperature of the slurry are well controlled in order to maximize the dissolution of Cl and K salts, and to minimize the dissolution of Na_2SO_4. The slurry is pumped to the centrifuge, which separates the solids (mainly Na_2SO_4, lean in Cl^- and K^+ ions) from the liquid (rich in Cl^- and K^+ ions, lean in SO_4). The solids, called *"Product"* at the mill, are fed to the black liquor mix tank for Na and S recovery. The liquid, called *"Reject"*, contains some suspended solids. It is fed into the reject tank, where about 2% is recycled back to the leaching tank, while the rest is purged to remove Cl and K from the system.

Cl and K Contents in Precipitator Ash

Figure 3 shows the Cl and K contents in the Boiler A precipitator ash from January 2000 to August 2004. The vertical line in the middle of the figure indicates the time when the ash leaching system was installed (May 2002). Originally, the Cl content varied widely between 9 and 14 wt%, with an average value of about 12 wt%. The K content was more stable at 6 to 8 wt%, with an average value of 7 wt%. After the ash leaching system was installed, the Cl content in the ash decreased markedly from 12 wt% to 7 wt% within the first 3 months, leveled at about 7 wt% in the subsequent 12 months to the end of 2003, and then decreased further to 5 wt% in the first half of 2004.

The K content also decreased slightly at first, from about 6.5 wt% to 5 wt%, then increased gradually back to the same level it was before the ash system installation. The variation in K content in the ash after the ash leaching system installation appears to be the same as that before installation, when the mill was purging ash. The results suggest that, while the ash leaching system may have lowered the Cl content in the Boiler A ash, it has not had much effect on the K content.

Ash, Water and Slurry Flow Rates

Figure 4 shows the mass flow rates of the precipitator ash from Boiler A, water and slurry processed through the ash leaching system since its start-up in May 2002. The flow rates show similar variations due to the careful control of slurry density between 1.3 kg/L and 1.4 kg/L.

The ash mass flow rate is essentially the slurry flow rate minus the water flow rate. It varied widely from 600 to 3000 kg/hr (or from 14 to 70 t/d), with an average value of about 40 t/d in 2002, 50 t/d in 2003, and 60 t/d in 2004. The increase in flow rates and their wide variations were due mainly to mechani-

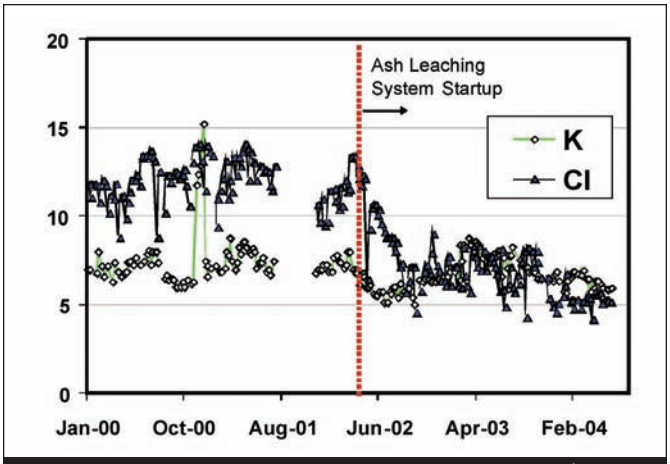


FIG. 3. Chloride and Potassium Concentrations (wt%) in Boiler A Precipitator Ash.

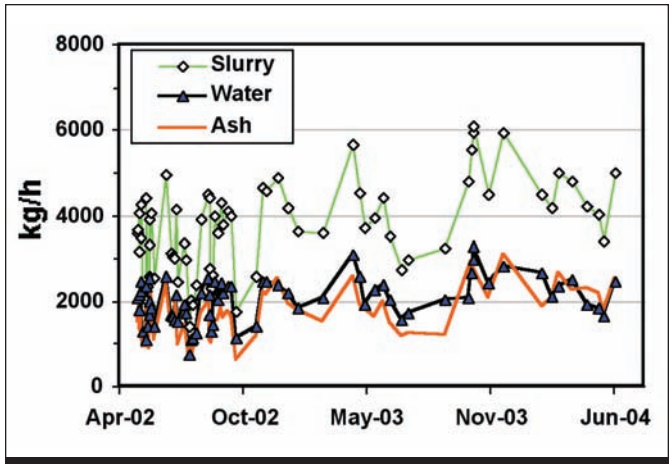


FIG. 4. Ash, Water, and Slurry Flow Rates fed into the leaching system.

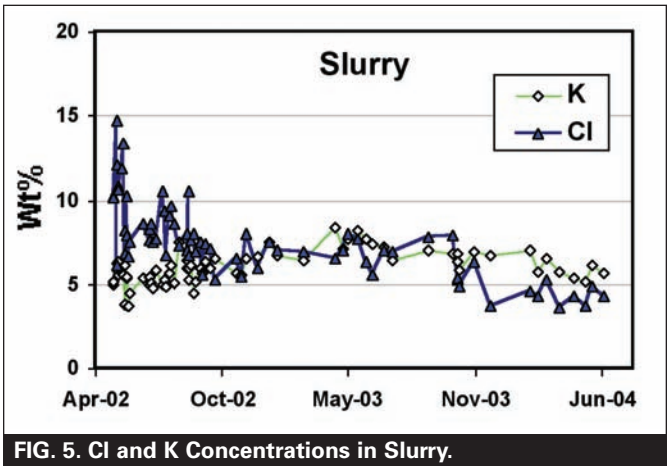


FIG. 5. Cl and K Concentrations in Slurry.

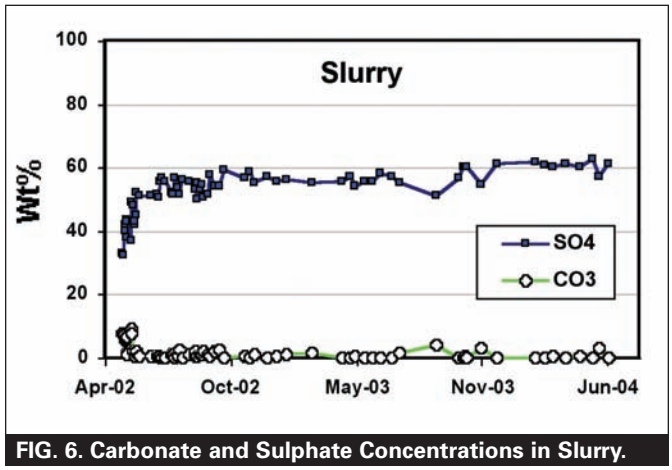


FIG. 6. Carbonate and Sulphate Concentrations in Slurry.

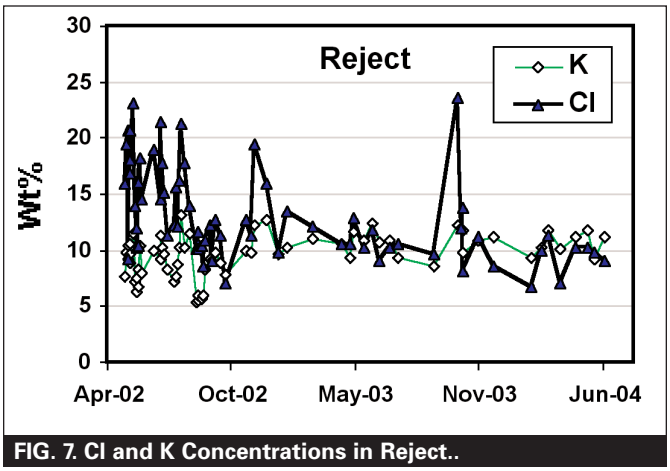


FIG. 7. Cl and K Concentrations in Reject..

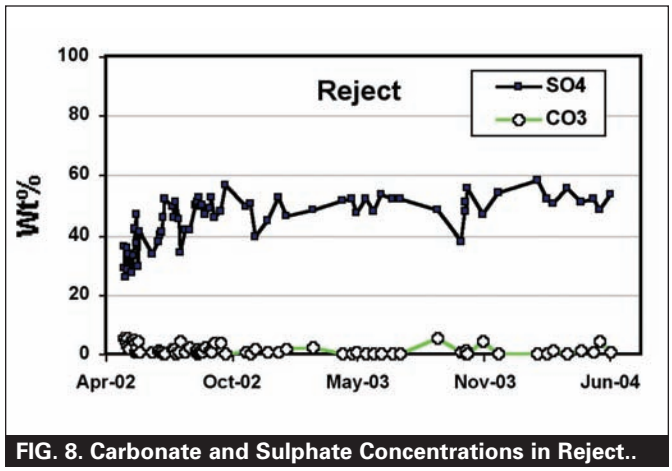


FIG. 8. Carbonate and Sulphate Concentrations in Reject..

cal problems with the slurry pump [2], and to the variation in black liquor firing rate of Boiler A.

Ash leaching system chemistry

Composition of Slurry

Since only a small amount (2%) of reject was recycled back to the leaching tank and the retention time in the leaching tank was short, the composition of the slurry is essentially the same as that of Boiler A ash. As shown in Fig. 5, the Cl and K concentrations in the slurry, in wt% (dry basis) are similar to that shown in Fig. 3 after the installation of the ash leaching system.

Figure 6 shows the corresponding CO_3 and SO_4 concentrations in the slurry. The CO_3 concentration in the slurry was high, 5 to 10 wt% prior to the ash leaching system installation. It then decreased rapidly after the system installation to an average value of about 1 wt% in 2003, and close to zero in 2004. The SO_4 concentration was much higher, about 30 wt% initially, but increased rapidly to about 50 wt% with-

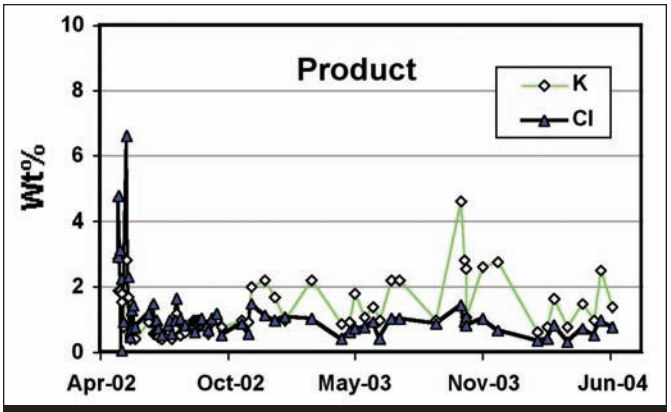


FIG. 9. Chloride and potassium contents in Product.

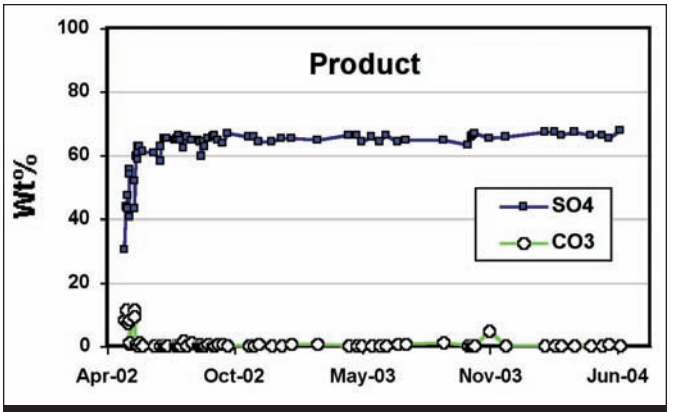


FIG. 10. Sulphate and carbonate contents in Product.

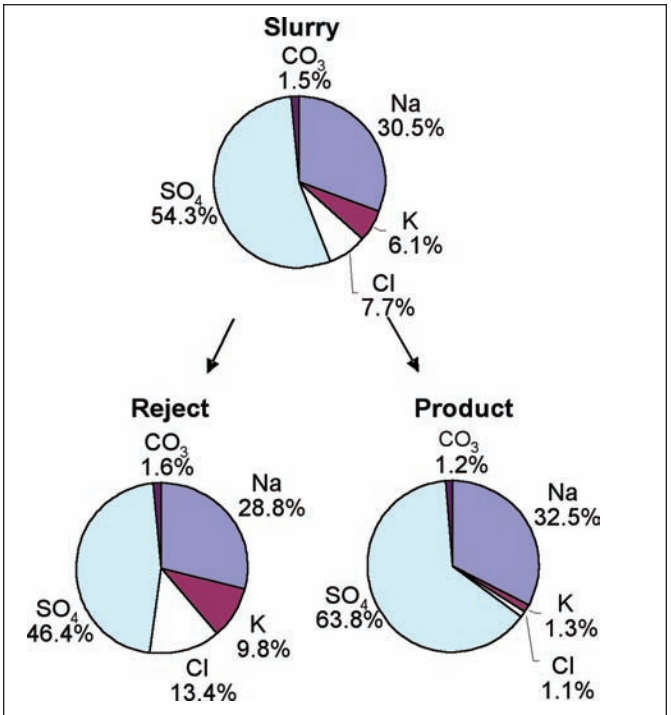


FIG. 11. Average Compositions of Slurry,Reject and Product over the past 2.5 years.

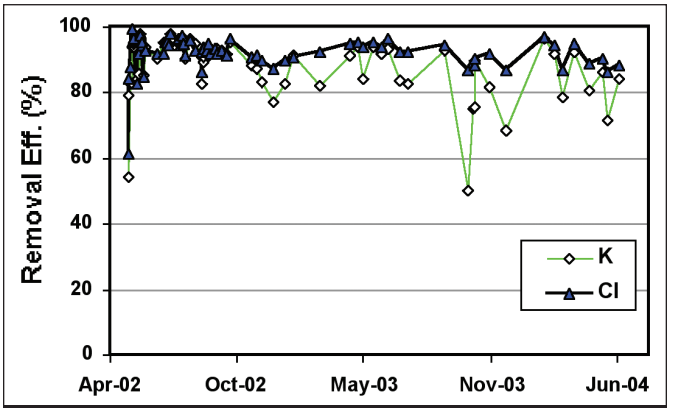


FIG. 12. Cl and K Removal Efficiencies of the Ash Leaching System.

in the first two weeks after the ash leaching system was installed. It has since increased steadily to about 55 wt% in 2003 and 60 wt% in 2004 at the expense of the Cl and CO_3 concentrations. Note that the 60 wt% is almost the maximum SO_4 concentration a precipitator ash could reach.

Compositions of Reject and Product

Figures 7 and 8, respectively, show the Cl and K concentrations and CO_3 and SO_4 concentrations in the reject. Compared to slurry, the reject contained more Cl and K, about 7 to 10 wt%, but less CO_3 and SO_4.

Figures 9 and 10, respectively, show Cl and K concentrations, and CO_3 and SO_4 concentrations in the product. Compared to both slurry and reject, the product was relatively pure, containing mostly Na_2SO_4 (>95%), with a small amount of Cl, K and CO_3.

The average compositions of slurry (or ash), reject and product during the past 2.5 year operation of the ash leaching system are shown in Fig. 11. It shows clearly that Cl and K are enriched in the reject, while they are diminished in the product.

Ash leaching system performance

The performance of the ash leaching system is determined by its ability to remove Cl and K from the ash (Cl and K removal efficiency) and its ability to recover Na and S in the ash (Na and S recovery efficiency). The Cl and K removal efficiencies are defined as follows:

$$Cl_{\text{Removal Efficiency}} = \frac{M_{Cl\,(\text{Slurry})} - M_{Cl\,(\text{Product})}}{M_{Cl\,(\text{Slurry})}} \times 100\%$$

$$K_{\text{Removal Efficiency}} = \frac{M_{K(\text{Slurry})} - M_{K(\text{Product})}}{M_{Kl\,(\text{Slurry})}} \times 100\%$$

where $M_{Cl\,(\text{Slurry})}$, $M_{K(\text{Slurry})}$, $M_{Cl\,(\text{Product})}$ and $M_{K\,(\text{Product})}$ are, respectively, the mass flows of Cl and K in the slurry and the mass flows of Cl and K in the product. These values can be obtained from the mass flow rates and compositions of slurry and product.

The Na and S recovery efficiencies are defined as:

$$Na_{\text{Removal Efficiency}} = \frac{M_{Na(\text{Product})}}{M_{Na(\text{Slurry})}} \times 100\%$$

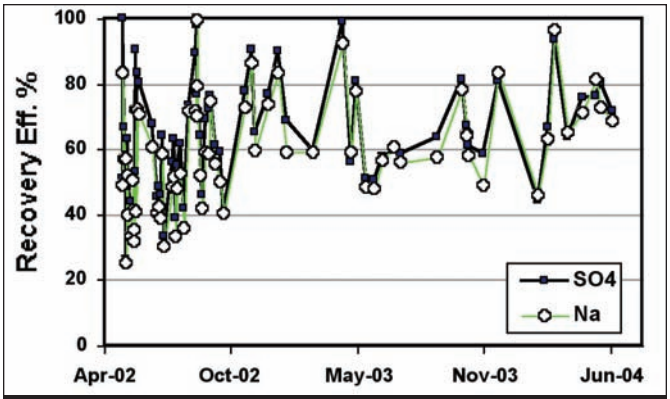


FIG. 13. Na and S Recovery Efficiencies of the Ash Leaching System.

$$S_{\text{Removal Efficiency}} = \frac{M_{SO_4(\text{Product})}}{M_{SO_4(\text{Slurry})}} \times 100\%$$

where $M_{Na\ (Slurry)}$, $M_{Na\ (Slurry)}$, $M_{SO4\ (Product)}$ and $M_{SO4\ (Product)}$ are, respectively, the mass flows of Na and SO_4 in the slurry and the mass flows of Na and SO_4 in the product.

The Cl removal efficiency of the system was high, averaging close to 90%. The K removal efficiency was somewhat lower, with an average value of about 80+ %, Fig. 12.

Figure 13 shows the Na and SO_4 recovery efficiencies. The values vary widely from 20% to 100% (no treatment), with an average value of about 65%. They also are very close to each other due to the fact that the product consists mostly of Na_2SO_4, as shown in Fig. 11.

It is important to note, from Figs. 12 and 13, that the Cl and K removal efficiency and the Na and S recovery efficiency are the opposite of each other. The higher the Cl and K removal efficiency, the lower the Na and S recovery efficiency becomes. In other words, if more Cl and K are removed, more Na and SO_4 will be lost.

Table I summarizes the average material balance for Cl, K, Na and S around the ash leaching system. The data clearly indicates that the ash leaching system at Aracruz has performed well, removing 90% of the Cl input and 82% of the K input to the system with the precipitator ash, while recovering an average of about 65% of the Na and S introduced with the ash.

Effect on overall mill chemical balance

The Cl and K contents of the Boiler A precipitator ash, shown in Fig. 3, were consistent with those of the black liquor, white liquor and precipitator ash from other two recovery boilers (B and C) at Aracruz. The data show that, while the chloride content in the ash (or mill liquors) has decreased considerably since the installation the ash leaching system, the potassium content has remained the same, despite the 80%+ K removal efficiency of the ash leaching system.

One possible reason for this finding is the high sulphidity operation adopted by the mill at about the same time as the installation of the ash leaching system. The white liquor sulphidity was increased from 32% (on AA) in June 2002 to 36% in August 2002. It was increased gradually to 40% over the subsequent 12 month period until August 2003, and has been kept at this 40% level since.

TABLE I. Average Cl and K Removal Efficiency and Na and S Recovery Efficiency of the Ash Leaching System.

	In t/d	Out t/d	Removal Efficiency %
Cl	3.0	2.7	90
K	2.6	2.1	82
	In t/d	**Out t/d**	**Recovery Efficiency ∞%**
Na	12	7.5	63
S	7.3	5.0	68

The substantial increase in sulphidity is expected to have had an impact on the mill chemical balance. It resulted in increased SO_2 emissions from the recovery boiler stack. More Cl would have been purged from the liquor system via HCl emissions, according to the following reactions:

$$2\ NaCl + SO_2 + 1/2\ O_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$$

$$2\ KCl + SO_2 + 1/2\ O_2 + H_2O \rightarrow K_2SO_4 + 2HCl$$

The resulting K_2SO_4 is thermally more stable and has a lower solubility in water than KCl. Furthermore, as the Cl content in the liquor decreases, there will be less Cl and K enrichment in the ash, and there will be less Cl and K for the ash leaching system to remove.

The net result is that the Cl concentration in the liquor and ash would be lower than that expected from the ash leaching system, while the K concentration would gradually increase. Nonetheless, the results indicate that the K concentration in the liquor cycle would have been higher if the ash leaching system was not installed.

Summary

The operating data of an ash leaching system at the Aracruz Celulose mill was analyzed to evaluate the performance of the system. The results show that:

- The ash leaching system at Aracruz has been performing well. It removes, on average, 90% of the Cl and about 82% of the K introduced to the system with the precipitator ash, while recovering about 65% of Na and S introduced with the ash.
- Despite the K high removal efficiency of the ash leaching system, the K concentration in the precipitator ash has remained at about the same level as that before the installation, when the mill was purging ash. The dramatic decrease in Cl concentration and the insignificant change in K concentration in the precipitator ash (and mill liquor) are likely a combined result of the installation of the ash leaching system and the operation of high white liquor sulphidity (40% on AA) of the mill.
- The high sulphidity operation helps remove more Cl from recovery boilers as HCl emissions. However, it also produces more K_2SO_4 in the precipitator ash which is much less water-

soluble than KCl. This makes K removal less effective.

Literature

1. TRAN, H.N., EARL, P. F. Chloride and Potassium Removal Processes for Kraft Pulp Mills: A Technical Review. Proc. International Chemical Recovery Conference, TAPPI/ PACTAC, Charleston, SC, June 7-10 (2004).
2. KNUTSOON, M., ERIKSOON, M., SARTORIO, L.C., HUBERT, V.R., FILHO, O.M., Experiences from first start-up of an ash leaching system. Proc. TAPPI Fall Technical Conference and Trade Fair 369-374, San Diego, CA (2002).

Résumé: Les résultats d'une analyse des données d'exploitation d'un système de lixiviation des cendres indiquent que le système a éliminé 90 % du chlore (Cl) et 82 % du potassium (K) introduit dans le système avec les cendres du précipitateur. La teneur en Cl des cendres a été substantiellement réduite par rapport à celle qui existait avant l'installation du système, tandis que la teneur en K est demeurée essentiellement la même que lorsque l'usine purgeait les cendres. La réduction importante de la teneur en Cl et le changement peu significatif de la teneur en K des cendres du précipitateur étaient probablement attribuables au système de lixiviation des cendres installé et au fonctionnement à haute sulfidité de l'usine.

Reference: GONÇALVES, C., TRAN, H., BRAZ, S., PUIG, F., SHENASSA, R. Chloride and potassium removal efficiency of an ash leaching system. *Pulp & Paper Canada* 109(3):T43-48 (March 2008). Paper presented at the 92nd Annual Meeting in Montreal, QC, February 6-10, 2006. Not to be reproduced without permission of PAPTAC. Manuscript received on June 01, 2006. Revised manuscript approved for publication by the Review Panel on December 18, 2007.

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