

# Closing Paper Mills' Operational Cycles: Next Steps Forward

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## ABSTRACT

With the consistent pursuit of pulp and paper mills towards closing the system cycles owing to environmental and economic necessities, the collateral effects of unwanted non-process elements building up in the liquor cycle is highly evident world-wide. Of these unwanted contaminants, the build-up of chlorides and potassium are of major concern to the Chemical Recovery Boiler, and offer the biggest challenge towards plant availability, plant maintenance, and plant efficiency.

Over a period of the years, the world has witnessed myriad technological advances, ranging from laboratory or pilot plant tests to commercial launch of the processes for removal of these elements. These processes are not only being implemented around the globe for new and existing mills, but are also proving their dramatic results. This paper highlights the technologies available as solutions for the industry to implement.

## Introduction

Chlorides and Potassium (commonly referred to as non process elements (NPEs)) enter into the process mainly from raw materials, water, and make-up chemicals, and recycle of bleach plant streams. The property of easy dissolution of salts of chloride and potassium in water, makes it difficult to remove these NPEs from the liquor cycle in closed systems (with focus towards high recovery efficiency), and inevitably they start building up.

The conventional and most popular method, being practiced today predominately in developing countries, of chloride and potassium removal has been dumping of ash collected from the recovery boiler electrostatic precipitators, from the area, where the concentration of these salts are found to be maximum. However, this mode results not only in the loss of valuable chemicals but also raises detrimental environmental concerns. With the tightening of air-emission norms, stack discharges have reduced, resulting in more of the recovered ash being recycled into the system.

The key ill effects of higher concentration of these two elements in the liquor cycles can be categorized as following:

- Fouling/plugging of heat transfer surfaces of recovery boilers causing loss of availability
- Corrosion of superheaters thereby limiting steam temperatures, which in turn affects power generation
- Increased soot blowing steam consumption
- Increase in dead load circulating in the system
- Lowering of black liquor heating value
- Affecting performance of electrostatic precipitator
- Increase in replacement and maintenance costs

- Reduction in overall recovery efficiency

This paper presents the problems associated with the high level of chloride and potassium and the possible ways of mitigating them.

## Fouling And Corrosion

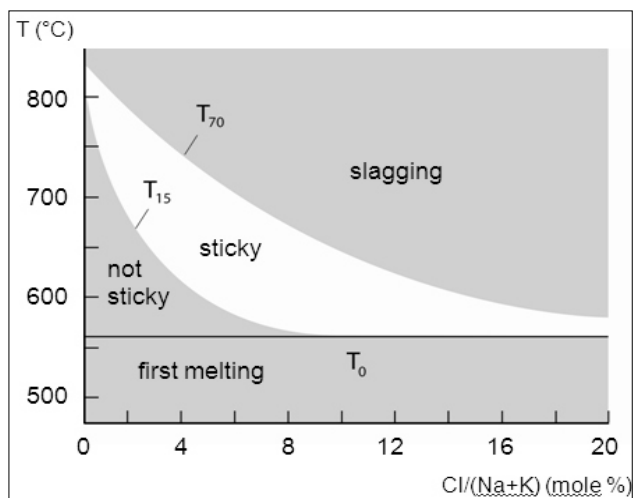
Of all the problems associated with build-up of chlorides and potassium in the liquor circuit, fouling of heat transfer surfaces and corrosion pose the highest threat.

The high content of chlorides leads to accelerated fouling and plugging in boiler while the high content of potassium leads to accelerated corrosion, especially in the superheaters. Fouling and plugging means higher soot blowing steam consumption, and lesser availability of the boiler. Increase in corrosion of superheater tubes means lowering the steam temperatures, with consequent loss in power generation, combined with high replacement costs.

The high content of chlorides affects  $T_{15}$  and  $T_{70}$ , leading to fouling and plugging in Boiler while the high content of potassium affects  $T_0$  leads to corrosion.

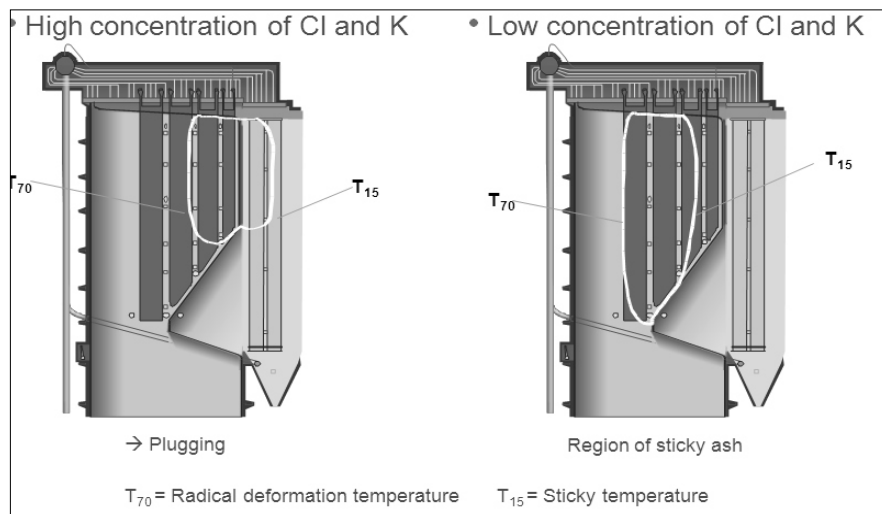
The melting temperatures can be calculated based on the composition of the deposits and, further, the composition of the deposits can be predicted quite reliably from the composition of black liquor. Hence, the maximum temperature of superheated steam can be determined if the Cl and K contents in black liquor are known. Therefore, if a boiler with a higher superheating is to be designed, the amounts of Cl and K need to be restricted (alternatively special alloys or exotic materials can be used for superheater but the cost becomes prohibitive). There are some methods to limit the Cl and K contents in the chemical cycle of the mill and the principles of those are described elsewhere.

**Figure. 1**  $T_0$ ,  $T_{15}$  and  $T_{70}$  Temperature as a function of ratio  $(Cl/(Na+K))$ , in mole%



The construction of the boiler pressure parts is a tactical act. The plant designer chooses a configuration such that the flue gas “sticky” temperature lies in a zone, where the cleaning of the heat-transfer surfaces is easy. As indicated in the above cases, it is advisable to have the sticky zone in the superheater area, as this area can be effectively cleaned by sootblowing. It is taken care not to have the sticky zone in the screen/boiler bank areas, which are more closely spaced, and thus difficult to clean.

**Figure. 2** Fouling scenario in higher/lower concentration of Cl and K



### Processes For Chloride And Potassium Removal

All of the commercially-available Cl and K removal processes treat precipitator ash from recovery boilers. They fall into four main categories: i) leaching, ii) evaporation/crystallization, iii) freeze crystallization, and iv) ion exchange.

The first three processes take advantage of differences in solubility between the various salts, primarily alkali sulfates

( $Na_2SO_4$  and  $K_2SO_4$ ) and alkali chlorides (NaCl and KCl), while the ion exchange process uses a proprietary resin which selectively adsorbs NaCl. The first three processes remove the Cl and K in a purge stream, and return the more purified alkali sulfate to the recovery liquor cycle, while in the ion exchange process, Cl removal is achieved, while K removal is negligible.

In both leaching and crystallization, the conditions which remove NaCl from  $Na_2SO_4$  also tend to remove  $Na_2CO_3$ , which represents a loss of valuable sodium, and hence an increased need for make-up caustic. The problem can be addressed by acidifying the leaching slurry or the crystallization mother liquor with sulfuric acid to convert the carbonate to more recoverable sulfate. However, this adds more sulfur into the system and affects the mill sulfur balance. Potassium removal is more complicated than that of Chloride because potassium can take different forms. Since mixtures of KCl and NaCl are more soluble than either of the pure salts, the presence of KCl does not pose a problem. However, potassium can also be present as  $K_2SO_4$ , or the double salt glaserite ( $3K_2SO_4 \cdot Na_2SO_4$ ) after dissolving and re-crystallization. These compounds tend to behave in a similar manner as  $Na_2SO_4$  in the system, i.e. the solubilities of  $K_2SO_4$  and  $3K_2SO_4 \cdot Na_2SO_4$  decrease as the concentration of K and/or Cl increases. This hinders the potassium removal in both the leaching and evaporation/crystallization processes, as potassium compounds remain insoluble during leaching, and re-precipitate during re-crystallization. In these situations, potassium can no longer be removed from the liquor cycle, and the concentration will continue to increase. When this is the case, the most effective solution may be to simply purge precipitator dust until the potassium concentration drops into a range where glaserite is no longer formed, and then begin operation of the removal system.

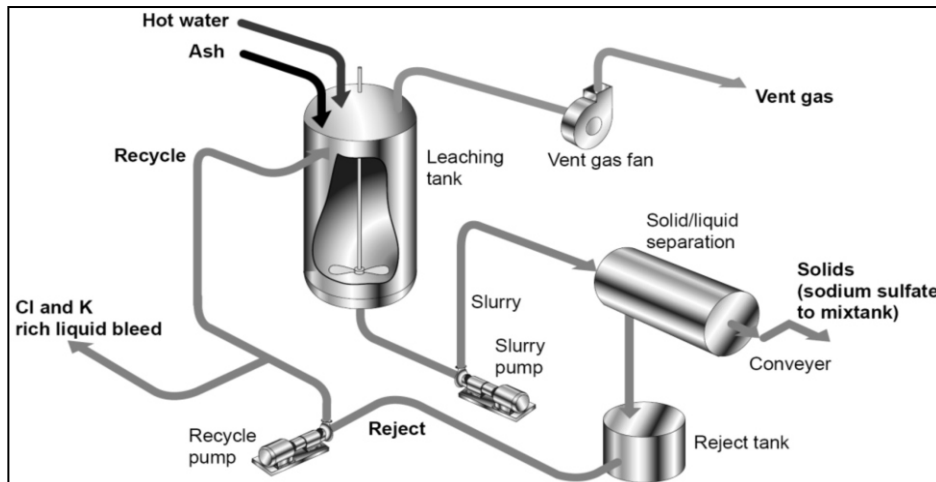
#### a. Leaching

Leaching takes advantage of the higher solubility of NaCl and KCl, compared to  $Na_2SO_4$ , especially in an NaCl-saturated solution. The leaching process consists of two main unit operations. In the first stage, precipitator ash is combined with water (and recycled leachate) to form a slurry. The amount of water/leachate used must be carefully controlled to promote the dissolution of chloride and potassium salts with least dissolution of sodium sulfate. A higher temperature also improves the selectivity of the process, as more Cl salts and less sulfate salts dissolve in the system. After mixing in a stirred tank, the slurry passes to the separation stage, typically a filter or centrifuge. The solids (primarily sulfate) are returned to the kraft liquor cycle, while the leachate (rich in Cl and K) is recycled back to the first step. A portion of the leachate is purged from the system as the means of Cl and K removal.

The advantage of leaching process is not only simple and confined to recovery boiler operation limits but also flexible, meaning ash leaching can be varied to achieve more or less K / Cl removal and Sodium sulphate recovery.

### i) Single Stage Ash Leach

Figure 3: Typical leaching process



In this process, 2 stage centrifuge is used where filtrate from centrifuge 2 is used counter-currently in leaching tank 2 and in leaching tank 1.

As can be seen from the above figure 5, sodium sulphate removal efficiency is optimized even at higher removal efficiency of K and Cl.

### b. Evaporation/Crystallization

Evaporation/crystallization processes also take advantage of the relatively low solubility of  $\text{Na}_2\text{SO}_4$ , as compared to the NaCl and KCl, but in the opposite manner to leaching. The precipitator dust is first dissolved in water (or recycled process condensate); the solution is then evaporated. Because of its lower solubility,  $\text{Na}_2\text{SO}_4$  crystallizes first.

The presence of Cl ions helps to decrease the solubility of  $\text{Na}_2\text{SO}_4$  further. The purified  $\text{Na}_2\text{SO}_4$  is filtered and returned as a solid to the liquor cycle. Most of the mother liquor (rich in Cl and K) is returned to the crystallizer, but a small portion is sewerred to purge the Cl and K.

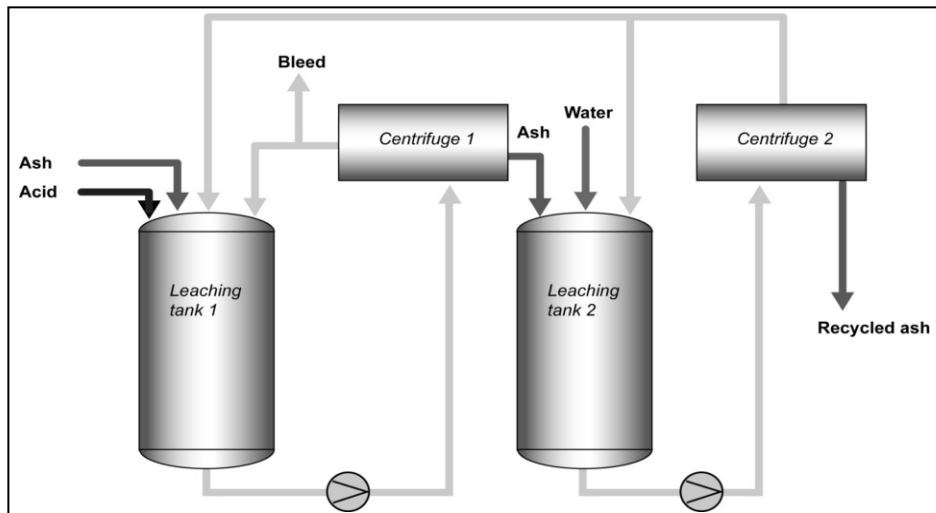
However, the single stage leaching process cannot achieve maximum removal and maximum recovery at same time as explained in figure 5:

### ii) Double Stage Ash Leach

In order to minimize the constraint as mentioned above in single stage ash leach process, a double stage ash leach process has been developed as explained in Figure 4 below.

There are three evaporation/crystallization processes available commercially. Although each uses a different evaporator design, the principle of operation is similar. All the processes use steam-driven evaporator/crystallizers, which may be single- or multi-effect, depending upon the design and integration with the pulp mill.

Figure 4: Typical Double Stage Ash Leaching Process



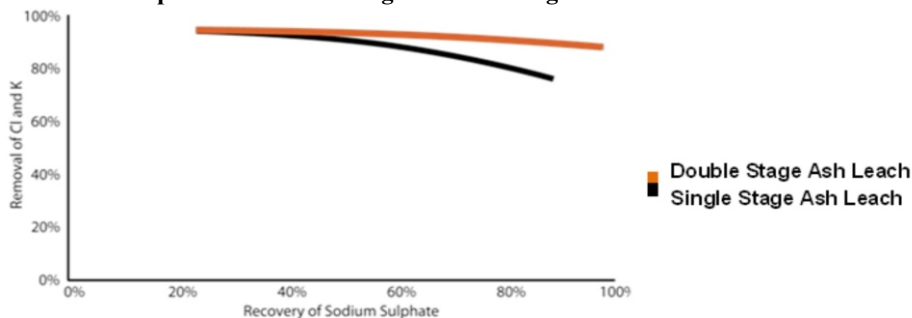
The advantages of crystallization process are better removal and recovery efficiency, and bigger crystal formation than that of precipitated  $\text{Na}_2\text{SO}_4$ . The disadvantage is higher energy consumption, as it is linked to the evaporation plant.

### c. Freeze Crystallization

Freeze crystallization relies on the dramatic decrease in solubility of sodium sulfate decahydrate ( $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ) at low operating temperatures. Below about  $30^\circ\text{C}$ ,  $\text{Na}_2\text{SO}_4$  suddenly precipitates as large  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$  crystals, leaving Cl and K in solution. The two phases can then be separated, with the purified sodium sulfate crystals returned to the kraft liquor cycle, and the solution purged to remove Cl and K.

The advantage of the freeze crystallization process is easy separation and fairly good Cl removal. While the disadvantage is higher energy consumption and possibly additional load on water evaporation.

Figure 5: Removal of Chloride and Potassium Vs Recovery of Sodium Sulphate for Double Stage Ash Leaching



#### **d. Ion Exchange**

Specialized ion exchange resins are commercially available which contain both cation- and anion-exchange groups on each particle, and so can remove both ions simultaneously. Because chloride ions are the only monovalent anions in the precipitator duct mixture, these resins will preferentially adsorb sodium chloride over sodium sulfate and carbonate.

Due to the sensitivity of the resin, the precipitator dust solution must be filtered beforehand, to minimize resin fouling. Regeneration is easily achieved with water.

One difference between the ion exchange process and other processes is that the purified sodium sulfate is returned to the kraft liquor cycle in the form of solution, and not as a crystal or slurry. If the mill has spare capacity in the black liquor evaporator train, then this will not be an issue, and in fact the ion exchange process could end up consuming less steam than an evaporation/crystallization process. However, if there is no additional black liquor evaporation capacity, this may necessitate an additional pre-evaporation stage, to minimize the water loading on the existing evaporators. The addition point of the sulfate solution to the black liquor evaporation train is also critical, since the relatively high concentration of carbonate could promote burkeite formation and scaling. One proposed alternative for the removal of chlorides from the recovery liquor cycle is to use ion exchange to treat a stream of oxidized white liquor, instead of the precipitator dust.

The advantages of ion exchange process are higher Chloride removal efficiency and minimal space requirements, while the disadvantage is that potassium removal is very poor.

#### **Conclusion**

Several processes are now available for the selective removal of chloride and potassium from the kraft recovery cycle. These processes can significantly decrease the Cl concentration in the liquor cycle, allowing for improved recovery boiler operation. Potassium levels are also decreased, but to a lesser extent.

All processes significantly decreases the Cl content to well below 1 wt% Cl. The leaching and crystallization processes also decreases the K content, while the ion exchange process has little effect on K levels. The time has come for the Indian paper mills to look into the direction of installing systems so as to solve the challenges associated with high levels of potassium and chloride in the black liquor cycle.

#### **References**

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