PROVEN METHODS for removing chloride and potassium from the recovery loop

In modern kraft recovery operations, the key sodium and sulfur compounds from the fiberline are recovered and regenerated to minimize the need for makeup chemicals — and to also produce renewable energy in the process. Chemical recovery loops are becoming more and more efficient such that emissions, effluents, and waste streams are minimized.

The tightening of these recovery loops creates new challenges as non-process elements (NPE) accumulate in the liquor circulation. Two of the most potentially harmful NPE are chlorides (Cl) and potassium (K). In high concentrations they can cause severe corrosion of recovery boiler heat exchangers. They also lower the melting temperature of the boiler fly ash, increasing fouling and potential for plugging the tight flue gas passages.

The traditional — and expensive — method of controlling the concentration of chloride and potassium is by dumping a portion of the ash from the boiler’s electrostatic precipitators (ESP). Dumping presents at least two very real issues: 1) two valuable process chemicals, sodium and sulfate, are dumped with ash, and 2) the dumping can create environmental concerns.

SELECTING THE MOST SUITABLE TECHNOLOGY

Selecting the most suitable technology for a mill is always case-specific, depending mainly on removal capacity needs and mill process characteristics.

The recovery of process elements and the removal of non-process elements is possible primarily due to the solubility differences between alkali sulfates and alkali chlorides. The general idea is that chloride and potassium are removed as liquids, while most of the valuable sodium and sulfate is recovered as solids and fed back to the chemical recovery cycle.

ASH LEACHING (ALE) TECHNOLOGY

For lower capacity requirements and generally for retrofit installations, the ALE process is less expensive to install and assembly is simpler. In ash leaching (Figure 1), the ESP ash is partially dissolved in hot secondary condensate from the evaporators. After partially dissolving, the solids and liquid are separated using a centrifuge. The solids consist mainly of sodium sulfate while the filtrate is rich in chloride and potassium.

After separation, the solids are mixed with heavy black liquor. A part of the liquid fraction is purged from the system to remove Cl and K. The rest of the filtrate is recycled to the leaching tank in order to prevent excess dissolution of sodium from the ESP ash.

Good solid-liquid separation is crucial, because the ash is only partially dissolved and the sodium sulfate particles in the ash are very small. A decanter centrifuge is employed for efficient solid-liquid separation. If the carbonate content of ESP ash is too high, sulfuric acid can be added to the slurry to convert the sodium carbonate to sodium sulfate. When ash is leached without acid addition, the more carbonate there is in ESP-ash the poorer is the separation — meaning that chloride and potassium rich liquid returns to the mill’s liquor cycle.

A typical ALE system has removal efficiency of 85% with a sodium loss of 25%. The best performance can be reached by optimization of the ash water ratio and recirculation to the leaching tank.

ASH RECRYSTALLIZATION (ARC) TECHNOLOGY

A typical ARC system has removal efficiency of 90% with a sodium loss of 20%. ARC technology can also handle larger capacities, making it the better choice for larger retrofits or greenfield installations.

In the ARC process (Figure 2), the ash is completely dissolved in clean condensate (or another calcium-free water source). After dissolving, the ash solution is pumped to a crystallizer where water is evaporated until sodium sulfate precipitates. The solids consist mainly of sodium sulfate while the filtrate is rich in chloride and potassium.

After separation, the solids are mixed with heavy black liquor. A part of the liquid fraction is purged from the system to remove Cl and K. The rest of the filtrate is recycled to the leaching tank in order to prevent excess dissolution of sodium from the ESP ash.

Good solid-liquid separation is crucial, because the ash is only partially dissolved and the sodium sulfate particles in the ash are very small. A decanter centrifuge is employed for efficient solid-liquid separation. If the carbonate content of ESP ash is too high, sulfuric acid can be added to the slurry to convert the sodium carbonate to sodium sulfate. When ash is leached without acid addition, the more carbonate there is in ESP-ash the poorer is the separation — meaning that chloride and potassium rich liquid returns to the mill’s liquor cycle.

A typical ALE system has removal efficiency of 85% with a sodium loss of 25%. The best performance can be reached by optimization of the ash water ratio and recirculation to the leaching tank.

ASH RECRYSTALLIZATION (ARC) TECHNOLOGY

A typical ARC system has removal efficiency of 90% with a sodium loss of 20%. ARC technology can also handle larger capacities, making it the better choice for larger retrofits or greenfield installations.

In the ARC process (Figure 2), the ash is completely dissolved in clean condensate (or another calcium-free water source). After dissolving, the ash solution is pumped to a crystallizer where water is evaporated until sodium sulfate pre-
Precipitates from the solution. Precipitated crystals are sent to a thickener and separated with a pusher centrifuge. Most of the separated liquid is recirculated to the crystallizer to minimize sodium losses. The remaining liquid is purged to remove dissolved chloride and potassium from the liquor cycle.

In new installations, the ARC process is usually integrated into the evaporation plant to decrease the fresh steam consumption of the crystallization process (an integrated system requires only 35-40% additional steam compared to a crystallizer operating standalone). Heat for the crystallizer can also be taken from flashed green liquor vapors, which might be a good option if there is a need for green liquor cooling.

**EXPERIENCE**

Operating a leaching or crystallizer type of chloride removal system is a trade-off between removal efficiency and sodium recovery, but generally ARC is more effective compared to ALE (Figure 3).

Potassium removal can be more challenging than chloride removal because of the formation of different solid potassium compounds. When the potassium mass fraction of ash is less than 3.5%, the removal efficiencies for chloride and potassium are quite similar. Higher potassium concentrations can form compounds that precipitate from the solution and decrease the removal efficiency.

Sufficient lowering of Cl and K levels in kraft recovery circulation can take several weeks or even months (Figure 4). Since the changes are not immediate, the chloride and potassium removal system can be shut down without interfering with recovery boiler operation. Also, if the need for Cl and K removal decreases over time, the system can be operated periodically to keep the concentrations at targeted levels.

**CONCLUSION**

The ALE process is relatively simple, and well proven. Its small footprint is ideal for retrofits and is more readily integrated into an existing recovery boiler layout. When the need for ash treatment capacity increases, the solid-liquid separation of the leaching system can become a bottleneck.

The ARC process is generally more suitable for larger chloride and potassium removal needs. Evaporated crystals are also predominantly pure sodium sulfate (Figure 5), so the recovery and removal efficiencies are also better.

**CONTACT**
Petteri Tiirikainen petteri.tiirikainen@andritz.com