
Cl+K removal in a Kraft Mill

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1. Introduction

High chloride (Cl) and potassium (K) concentration in black liquor increases the risk for corrosion and plugging in recovery boilers. The liquor cycles in modern pulp mills are well closed meaning increased NPE concentrations also in black liquor. Investment in high energy recovery boiler with high power production is often very feasible. Due to recent changes in cost effectiveness, caused by higher energy efficiencies and higher energy prices, more than dozen pulp mills are today controlling their chloride and potassium concentrations by ash leaching or crystallization. Low Cl+K concentrations are needed to avoid increased failure when going for high efficiency boiler systems, working at high steam temperature.

The selection between Cl+K removal processes has to be done considering:

- Chloride and potassium input
- Capacity
- Ash and black liquor composition
- Target chloride and potassium concentration in black liquor / ESP ash
- Removal efficiency
- Investment costs
- Mill balance (sodium / sulfur)
- Make-up chemical prices

Chloride and potassium are enriched in electrostatic precipitator ash and therefore ESP ash is a favorable stream to process when aiming to control the chloride and potassium content of the whole Kraft liquor cycle. In the paper three different commercial chloride control methods are described and compared.

- Ash out take (dumping)
- Leaching
- Ash crystallization

In all the chloride removal methods also valuable ESP ash chemicals will be lost. Because main part of ESP ash consists of valuable process chemicals, sodium sulfate and sodium carbonate, the value of sodium losses has to be accounted for. The sodium losses depend in addition to the selected process and chloride input to the mill also on the required chloride + potassium removal, Cl + K concentration in the ash (or in black liquor). The performances of the three processes are presented as a function of required chloride removal rate and Cl-concentration in the ash.

2. Effect of chloride and potassium content on recovery boiler fouling

Composition of dust from recovery boiler furnace (ESP ash) varies much depending on liquor properties and firing conditions including the heat load of the super heaters', and especially of the concentration of the potassium and chloride in the firing black liquor. In Table 1 is the range of major components in ESP ash presented.

Table 1. Typical composition range of ESP ash

Component	wt-%	Compound	wt-%
Na	28 - 35	Na ₂ SO ₄	65 - 90
SO ₄	45 - 65	Na ₂ CO ₃	9 - 27
CO ₃	5 - 15	NaCl	2 - 10
K	2 - 10	K ₂ SO ₄ KCl	5 - 20
Cl	1 - 5		

The tendency of ash to form deposits, is related to, the smelt behavior of the ash. Smelting curve depends on ash composition, generally a high chloride and potassium concentration causes low sticky temperature T_{15} , therefore high Cl+K requires, to avoid fouling and corrosion, low steam temperature to obtain low surface temperature for the superheater pipes.

Figure 1, is an example, of the effect of chloride and potassium content on the sticky temperature T_{15} (figure concentrations are given as a mole ratio of either Cl or K per alkali metals (Na + K)).

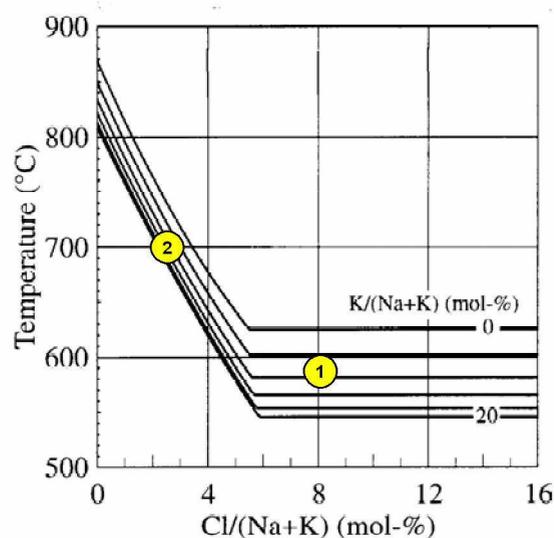


Figure 1. Sticky temperature T_{15} as function of chloride and potassium content in ESP ash
 Point 1. Ash Cl-content = 8 mol-% (4 wt-%) and K = 9 mol-% (5 wt-%) => T_{15} = 580 °C.
 Point 2. Cl = 2 mol-% (1 wt-%) and K = 3,6 mol-% (2 wt-%) => T_{15} = 700 °C

In practice some safety margin for the maximum allowed temperatures has to be reserved. Generally, the following maximum chloride and potassium concentrations (Table 2.) are recommended:

Table 2. Recommended maximum weight % for Cl and K

Steam	Virgin BL		ESP ash	
Temp. / °C	Cl / %	K / %	Cl / %	K / %
< 480	0.5	1.5 - 3	2.5	4 - 7
< 500	0.2 - 0.3	1 - 2	1 - 1.5	2.5 - 5
> 500	0.15	1 - 2	1 - 1.5	2.5 - 5

To make detailed estimation for “safe, non-fouling” maximum chloride and potassium content, boiler CFD calculations including temperature profile and smelt curve for the ash have to be done.

Depending on construction materials risk for chlorine corrosion may be the limiting factor to maximum allowable temperature.

3. Chloride and Potassium sources and losses in liquor cycle

The NPE input sources and losses in liquor cycle are listed in Table 3. Cl- and K-input from wood depends largely on the soil and transportation (e.g. sea floated). Flue gas losses are connected to SO₂ emissions, the higher liquor DS the lower SO₂ and Cl emissions, with DS over 75 % the losses are practically zero.

In euca mills typical net input for chloride is 1 – 3 kg Cl /ADT and for potassium 2 – 5 kg K / ADT and for the soft wood respectively 0,3 – 1 kg Cl /ADT, 1 – 2 kg K / ADT.

Table 3. Chloride and potassium sources and losses

Source	kg Cl / ADt	kg K / ADt
Wood	0.2 – 3	0.4 – 3
Make up chemicals and water	0.2 – 0.8	
Waste acid	0.1 – 0.5	

Losses	kg Cl / ADt	kg K / ADt
Washing losses	0.1 – 4	0.2 – 3
Flue gases	0.01 – 0.5	

4. Chloride and potassium enrichment in ESP ash

Chlorides and potassium compounds have higher vapor pressures than sodium sulfate. This results in their preferential volatilization from the smelt bed into the ash stream. As a result, chloride and potassium have higher concentrations (of DS) in ash than in virgin black liquor.

The enrichment is usually defined as the ratio of the content in the dust to the content in the virgin black liquor. In the calculation the contents are expressed as the molar ratio of chloride and respectively of potassium to the sum of sodium and potassium, enrichment factors for Cl and K in Equations 1 and 2. Concentrations in the equations are expressed as mol-%.

$$E_{Cl} = [Cl / (Na + K)]_{ash} / [Cl / (Na + K)]_{virgin\ BL} \quad (1)$$

$$E_K = [K / (Na + K)]_{ash} / [K / (Na + K)]_{virgin\ BL} \quad (2)$$

Cl and K enrichment factors vary very much (Table 4) depending on liquor properties, potassium and chloride concentrations and firing conditions, and especially on heat load.

Table 4. Enrichment factors

NPE	Range mol/mol	Typical mol/mol
Chloride	0.3 - 6	2.6
Potassium	1 - 2.5	1.6

Rough estimate for typical enrichment factors on weight basis for chloride = 5 and for potassium = 2.5. E.g. If Cl in virgin liquor = 0.5 wt-%, Cl in ash = 2.5 wt-%.

5. Chloride and potassium removal methods

Nowadays chloride and potassium content in ESP ash is controlled by:

- 1) Ash out-take (dumping)
- 2) Ash leaching
- 3) Ash crystallization, Andritz Ash ReCrystallization, ARC

Ash dumping is widely used in the industry, no need or low investment costs but chemical losses are high. The two other methods are based on solubility differences between different ash components: chloride and potassium compounds are more soluble than sulfates and carbonate.

5.1 Ash leaching

In leaching process (Figure 2.) ESP ash is mixed with hot water in ratios of 1 – 1.5 kg ash / kg water forming slurry: ash is only partially dissolved in water. Most of chloride and potassium compounds are dissolved in water while major part of sodium sulfate and carbonate remain as solids in the slurry. The slurry is pumped from the mixing tank to a decanter centrifuge that separates solids and liquid. The filter cake is returned to black liquor mix tank and the filtrate, enriched in chloride and potassium is purged to sewer.

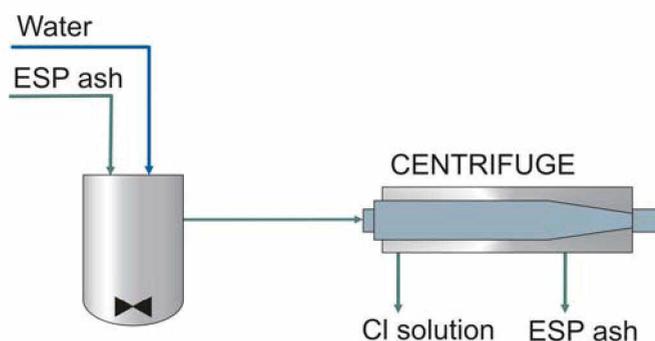


Figure 2. Principle of Ash Leaching

When carbonate (CO_3) concentration in the ash is over 5 %, the settling velocity of the slurry particles becomes very low and the ash cake remains very wet, meaning that Cl and K removal rates are decreased. The carbonate concentration can be decreased by adding sulfuric acid in the leaching tank decreasing pH from 10 to 11 down to 8.5 to 9. The acid reacts then with carbonate forming sodium sulfate and carbon dioxide according to the formula below:



The acid consumption depends on the carbonate content in the ash. For example: if the untreated ash contains 10 % carbonate ca. 80 kg sulfuric acid / ton of ash is required to decrease the carbonate concentration down to 5 %. The added acid is not wasted; it compensates partially the need of sodium sulfate make up to the liquor cycle.

5.2 Ash crystallization, ARC

In crystallization process ESP ash is first dissolved completely in hot water (or condensate) in ratios of 0,3 – 0,6 kg ash / kg water. The solution is fed to evaporative crystallizer where most of sodium sulfate and carbonate is crystallized and most of chloride and potassium compounds remain in the solution. The crystal slurry is pumped from the crystallizer to the centrifuge where crystals and liquid are separated. The filter cake is returned to black liquor mix tank and the filtrate, enriched in chloride and potassium is purged to sewer.

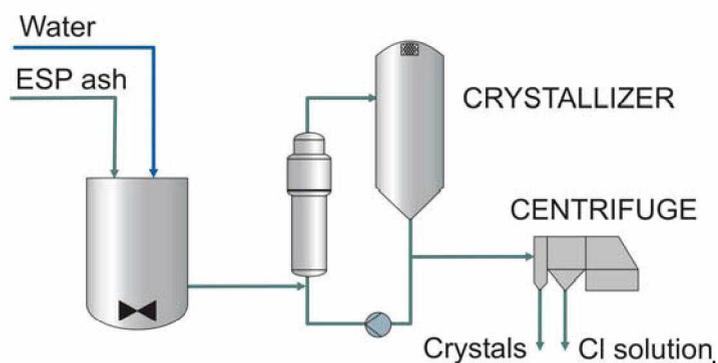


Figure 3. Principle of Ash Crystallization.

6. Metal ions in the removal process

ESP ash water solution has pH 10 -11. Most metal ions form insoluble hydroxides in basic solutions and therefore metals in the ash are returned back to liquor cycle with centrifuged cake from the removal process and only 2 – 15 % is purged to the sewer or otherwise: 85 – 98 % of metals are recovered.

Table 5. Measured metal concentrations in an ARC process

		Virgin BL	Esp Ash	Crystals from ARC	Purge from ARC
Al	mg/kg ds.	< 200	39.4	37.0	2.96
Cd	mg/kg ds.	< 0.4	0.28	0.41	< 0.05
Co	mg/kg ds.	< 2	0.15	0.26	0.10
Pb	mg/kg ds.	< 4	9.94	17.4	0.24
Mg	mg/kg ds.	345	168	97.8	15.8

7. Comparison of chloride and potassium removal processes

Chloride and potassium removal efficiency depends on ash composition and is related to chemical losses in each controlling method, part of the process elements and compounds are purged with Cl and K to sewer. Typical chloride removal efficiency for leaching and crystallization processes is presented in figure 4 as a function of sodium losses.

Potassium removal efficiency is about the same as that for chloride when potassium content in the ash is less than 4 wt-%. In higher potassium concentration glaserite, $K_3Na(SO_4)_2$, co-crystallizes with sodium sulfate and potassium removal will be decreased remarkably. So when a Cl&K removal process is installed in an existing mill with high potassium content, ash has to be taken out until the potassium concentration in ESP ash has decreased to about 4 %.

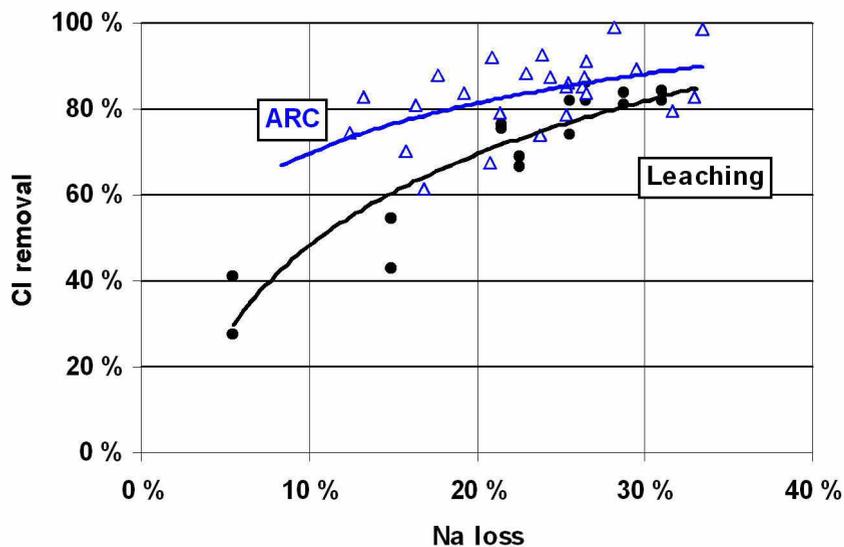


Figure 4. Chloride removal efficiency as a function of sodium losses.

Figure 4 shows that the crystallization process is much more effective and has less chemical losses than the leaching process. Depending on the required chloride and potassium content in ash and the input of Cl and K into the liquor cycle, will we in most cases only need to treat a part of the ash to reach an acceptable concentration for Cl+K. In such cases, will the efficiency of the Cl + K removal process, with respect to the chemical losses, have a less significant role to determine the process alternative that is most cost effective.

While each pulp mill has different ash composition Andritz has developed a comprehensive liquid-solid equilibrium program by which the two processes can be simulated and the optimum process alternative for the specific case can be selected.

In Table 6 is the Ash Re-Crystallization (ARC) and leaching processes compared with respect to the ash out-take.

Table 6. Comparison of Cl + K removal processes

Mill data			ESP Ash	
			Component	wt-%
Pulp production	ADt/d	2 000	Na	32.5
Recovery Boiler	ton DS/d	3 500	K	2.7
K removal	kg/ADt	1.1	Cl	1.0
	ton/d	2.3	SO ₄	53.8
Cl removal	kg/ADt	0.4	CO ₃	10.0
	ton/d	0.9		
Process		ARC	Leaching	Out take
ESP ash feed	ton/d	108	111	87
of ash	%	39	40	31
Removal (of treated ash)				
K	%	90	78	100
Cl	%	90	84	100
Loss				
Na (of treated ash)	%	20	30	100
	ton/d	7	10	28
	kg/ADt	3.5	5.2	14
SO ₄	ton/d	6	16	47
	kg/ADt	2.9	8.1	23
Make up chemicals (100%)				
H ₂ SO ₄	ton/d	-	8.6	-
	kg/ADt	-	4.3	-
Na ₂ SO ₄	ton/d	11.7	8.7	68.8
	kg/ADt	5.9	4.4	34
NaOH	ton/d	7.3	11.6	10.2
	kg/ADt	3.7	5.8	5
SO ₄	%	15	23	100

Investment costs for ash out-take is much lower than the other removal processes in Table 6, but the annual make up chemical costs are very high. Depending on mill sulfur and sodium balances the share of the make up chemicals may be different from the figures shown in the table. Generally the pay back time for the investment costs of ARC or leaching is less than one year compared to total out take costs.

Comparing ARC and leaching processes with the same Cl and K target for (virgin liquor / ESP ash) chloride and potassium concentrations:

- Make up chemical costs for ARC is lower due to higher Na and SO₄ recovery
- Electrical power consumption is about same
- Heat consumption in leaching is much lower

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- Different secondary heat sources (green liquor flash steam, integration with black liquor evaporator) can be utilized in ARC
 - Investment cost for leaching is lower

8. Summary

The liquor cycles in modern pulp mills are well closed meaning increased NPE concentrations also in black liquor. Investment in high energy recovery boiler with high power production is often very feasible. Due to recent changes in cost effectiveness, caused by higher energy efficiencies and higher energy prices, more than dozen pulp mills are to-day controlling their chloride and potassium concentrations by ash leaching or crystallization.

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