



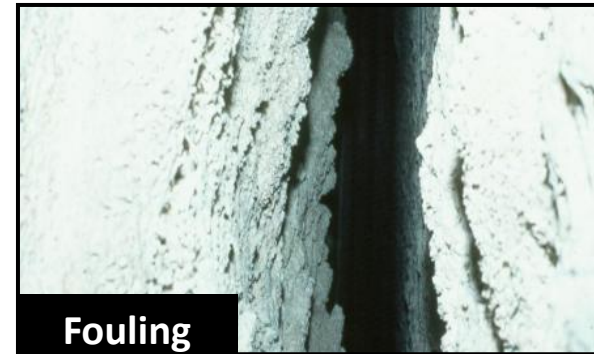
The Roles of Potassium in Kraft Recovery Operations

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K (Potassium)

- K, along Cl (chlorine/chloride), has long been considered as an undesirable non-process element (NPE) in the recovery process
- It lowers $T_{\text{First Melting}}$ of RB deposits
→ Superheater corrosion
- It lowers T_{Sticky} of carryover
→ Fouling of tube surfaces/plugging of gas passages
- Same as Cl, K is controlled by ash PURGING and/or ash TREATMENT due to its enrichment in the ESP ash



The Problems

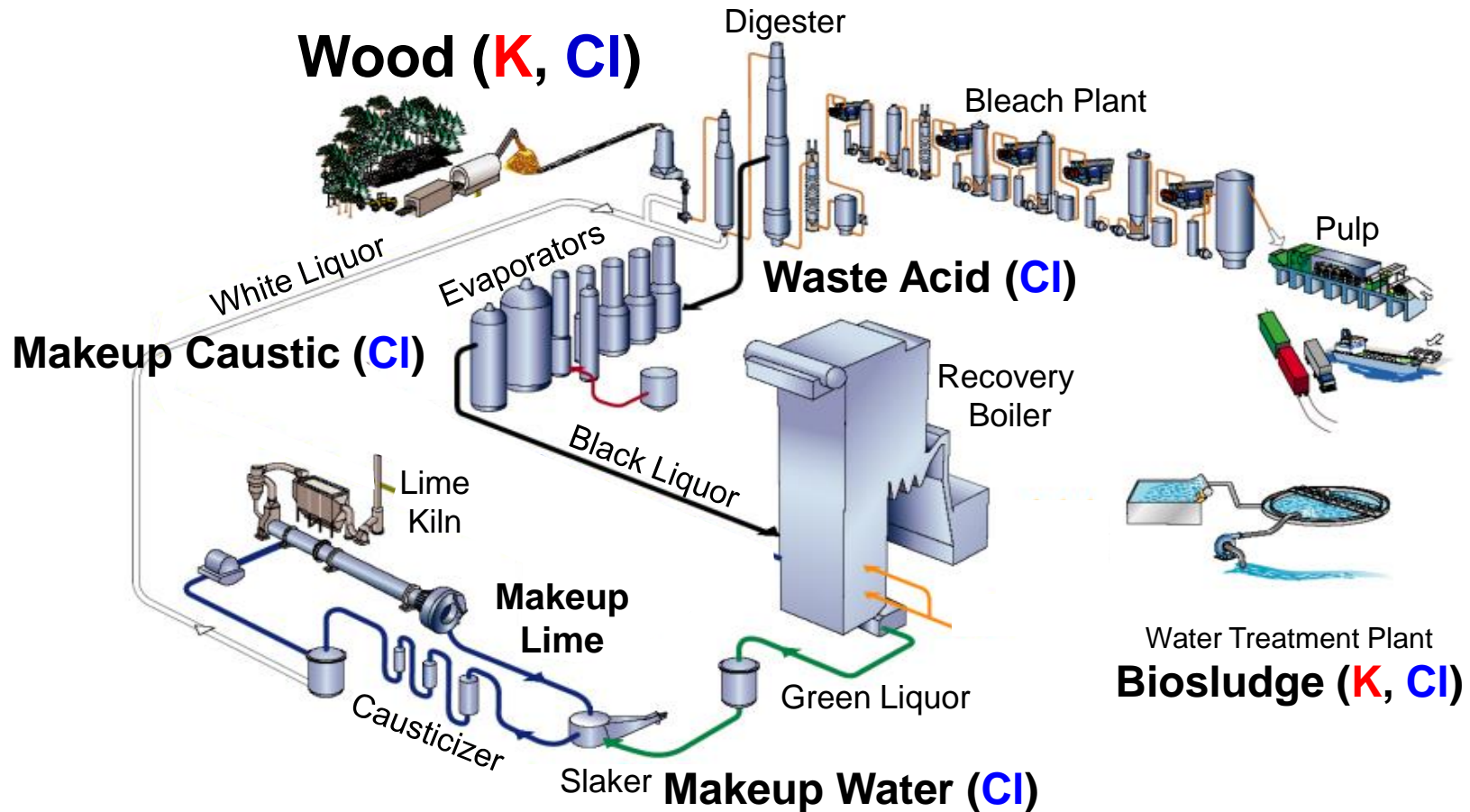
- Ash purging effectively removes not only Cl and K, but also Na and S, resulting in substantial chemical losses.
- Ash treatment systems can control Cl well, but not K.
- Depending the type of treatment technology employed, Cl content in black liquor can be kept under 0.2 wt% ds, but K content can remain high, 4 to 5 wt% ds, in some cases.
- Should a high K content in the liquor cycle be a concern?

➔ *To answer this question, it is important to understand how K may affect recovery operations.*

Presentation Outline

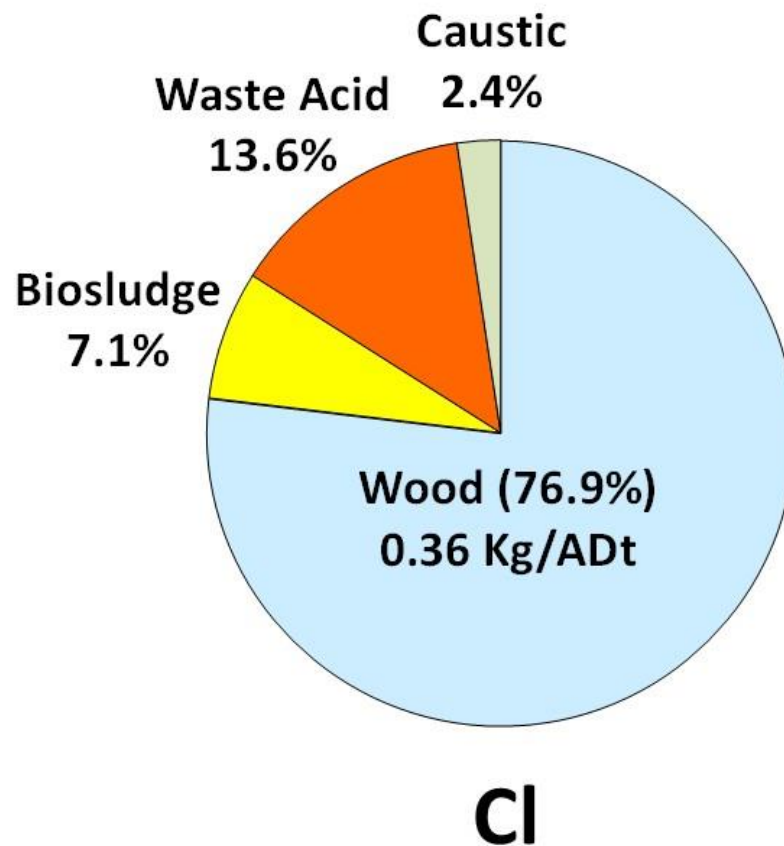
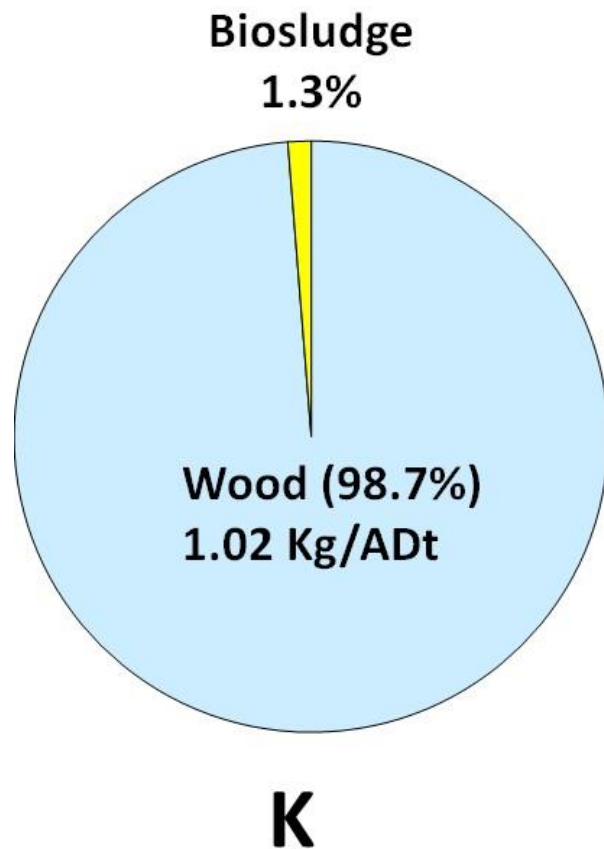
- Sources of K and Cl in kraft pulp mills
- How do K and Cl accumulate?
- Is K a process element or a non-process element?
- Impact of K on recovery operations
- Summary

Sources of K and Cl in Pulp mills



(Drawing: Courtesy Valmet)

Sources of K and Cl in Finnish Mills



Salmenoja, K., et al., ICRC (2004)

How Do K and Cl Accumulate?

● Accumulation Factors (AF)

$$AF_{\text{Liquor Cycle}} = \frac{E_{\text{WhiteLiquor}}}{\sum E_{\text{Input}}}$$

$$AF_{\text{Lime Cycle}} = \frac{E_{\text{LimeMud}}}{\sum E_{\text{Input}}}$$

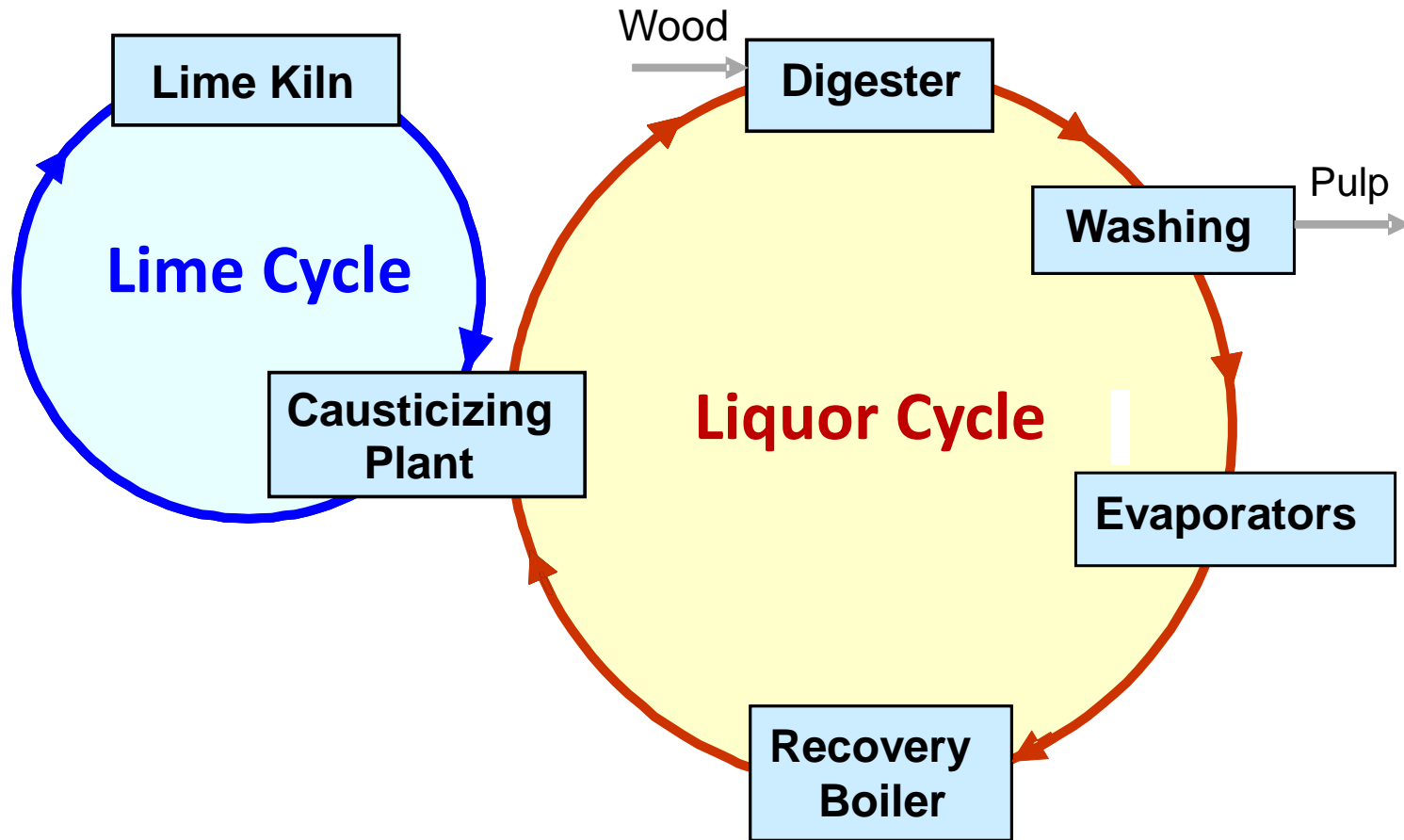
AF: Accumulation factor of an NPE in the liquor cycle or lime cycle

E: Amount of that NPE in white liquor or lime mud (kg/ADt pulp)

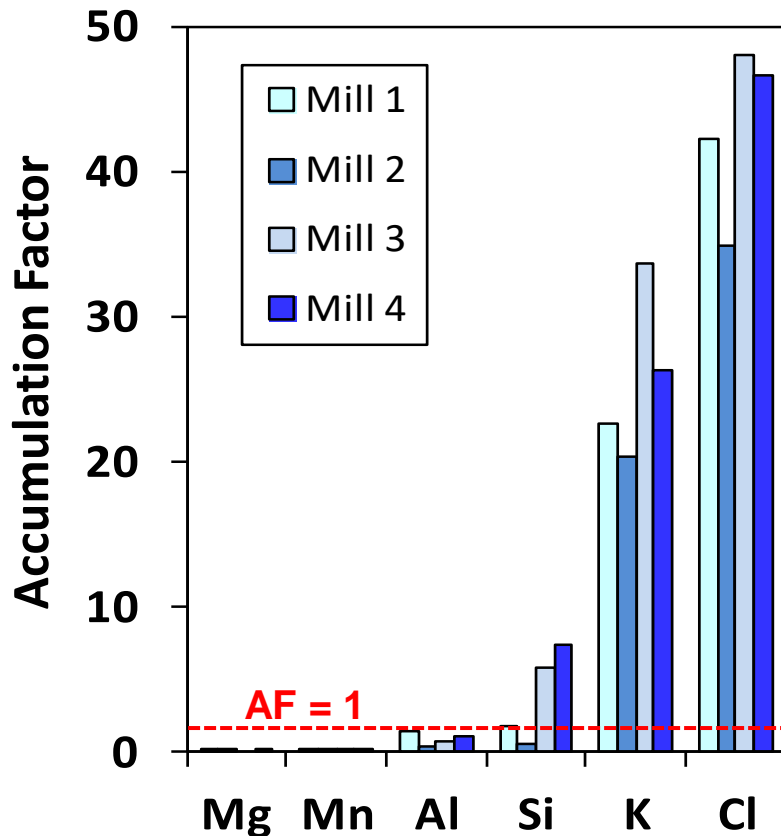
$\sum E_{\text{input}}$: Total amount of that NPE introduced into the recovery system from all sources (kg/ADt pulp)

Accumulation factor of an NPE is governed mainly by the solubility of compounds made of that NPE in green/white liquor

Main Cycles in the Recovery Process

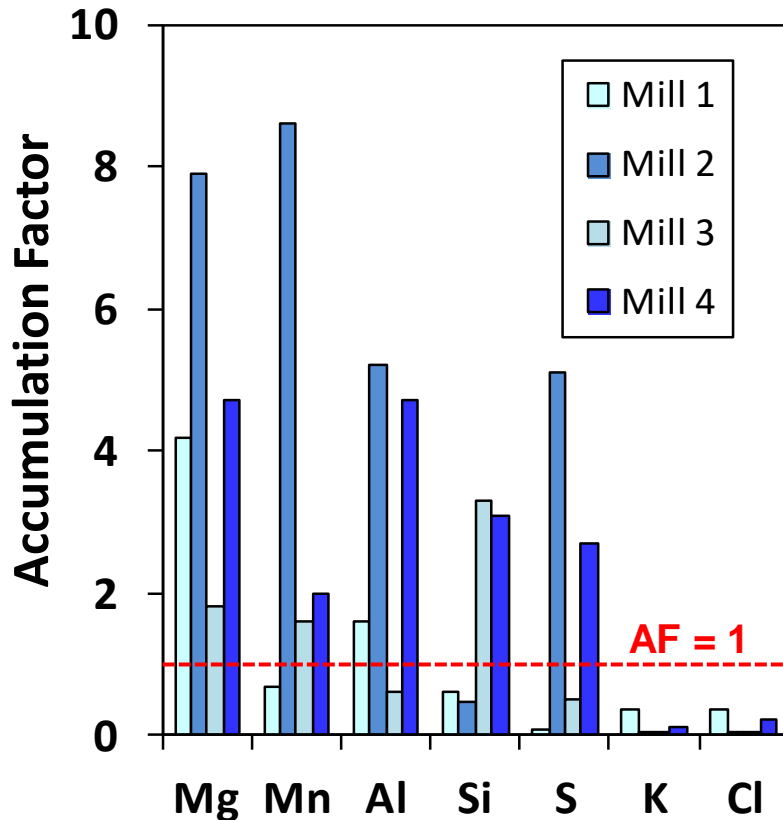


Accumulation of NPEs in **Liquor** Cycle



- NPEs accumulate only if $AF > 1$
- Cl accumulates more than 40 times of its total input
- K also accumulates, but less than Cl
 - K-compounds are less soluble
- Si and Al accumulate only slightly
- Mg and Mn do not accumulate

AF of Common NPE in Lime Cycle



- Opposite trend of liquor cycle
- Mg, Mn, Al, Si and S accumulate
- K and Cl do not S accumulate

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- Sources of K and Cl in kraft pulp mills
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Liquor Chemistry

- Green/white liquor contains

- Anions: CO_3^{2-} , S^{2-} , SO_4^{2-} , OH^- , Cl^-

- Cations: Na^+ , K^+

- Σ moles of anions = Σ moles of cations

$$\frac{\text{CO}_3}{60} + \frac{\text{S}}{32} + \frac{\text{SO}_4}{96} + \frac{\text{OH}}{34} + \frac{\text{Cl}}{71} = \frac{\text{Na}}{46} + \frac{\text{K}}{78}$$

$$\left[\frac{\frac{\text{CO}_3}{60} + \frac{\text{S}}{32} + \frac{\text{SO}_4}{96} + \frac{\text{OH}}{34}}{\frac{\text{Na}}{46} + \frac{\text{K}}{78}} \right] + \left[\frac{\frac{\text{Cl}}{71}}{\frac{\text{Na}}{46} + \frac{\text{K}}{78}} \right] = 1$$

Liquor Chemistry

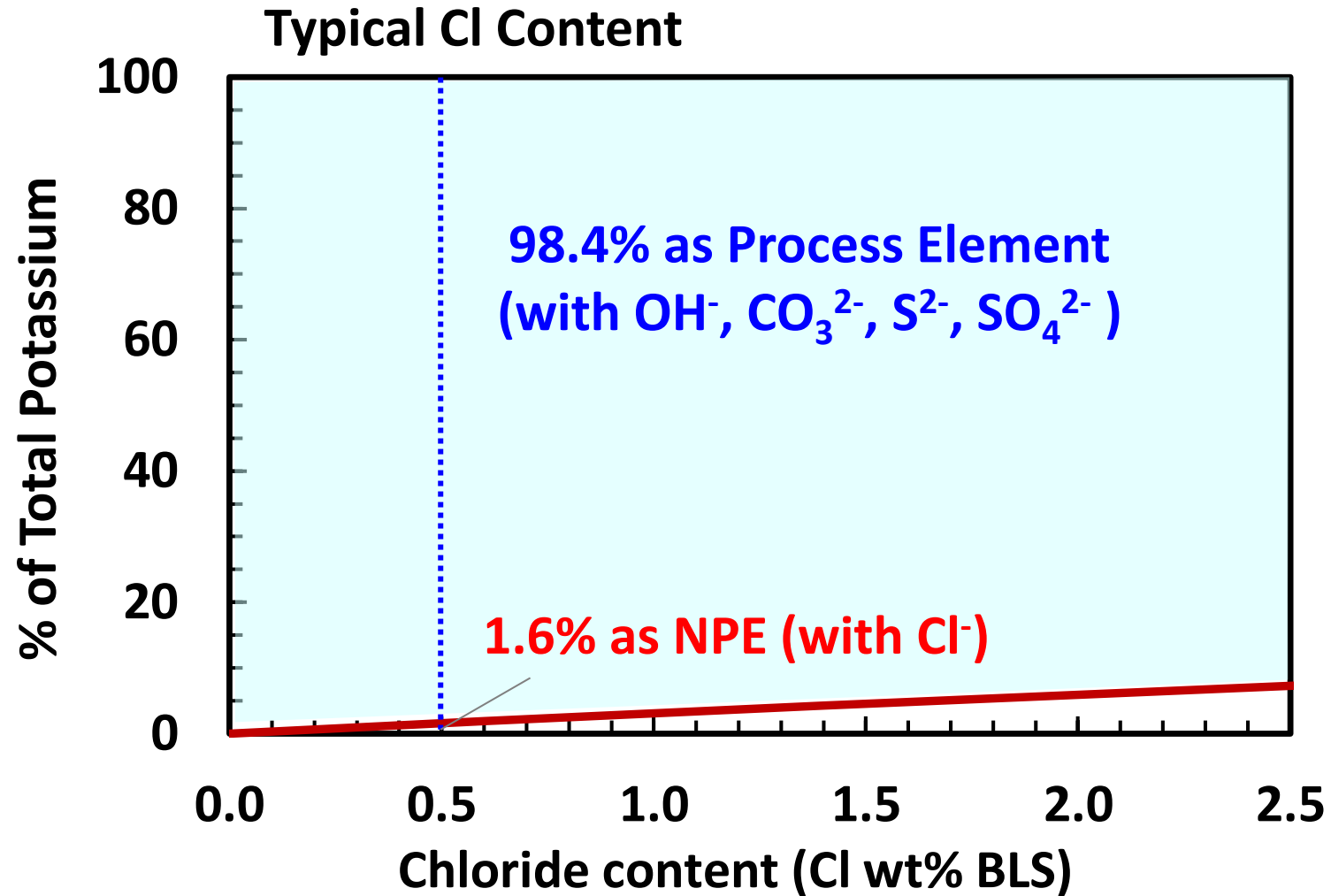
$$\boxed{\frac{\frac{\text{CO}_3}{60} + \frac{\text{S}}{32} + \frac{\text{SO}_4}{96} + \frac{\text{OH}}{34}}{\frac{\text{Na}}{46} + \frac{\text{K}}{78}}} + \boxed{\frac{\frac{\text{Cl}}{71}}{\frac{\text{Na}}{46} + \frac{\text{K}}{78}}} = 1$$

Process Element

Non-Process Element

- K⁺ connected with CO₃²⁻, S²⁻, SO₄²⁻ and OH⁻ is process element
- K⁺ connected with Cl⁻ is non-process element

K Distribution in Green/White Liquor



Precipitator Ash Chemistry

- Ash contains

- Anions: CO_3^{2-} , SO_4^{2-} , Cl^-

- Cations: Na^+ , K^+

- Σ moles of anions = Σ moles of cations

$$\frac{\text{CO}_3}{60} + \frac{\text{SO}_4}{96} + \frac{\text{Cl}}{71} = \frac{\text{Na}}{46} + \frac{\text{K}}{78}$$

$$\left[\frac{\frac{\text{CO}_3}{60} + \frac{\text{SO}_4}{96}}{\frac{\text{Na}}{46} + \frac{\text{K}}{78}} \right] + \left[\frac{\frac{\text{Cl}}{71}}{\frac{\text{Na}}{46} + \frac{\text{K}}{78}} \right] = 1$$

Process
Element

Non-Process
Element

Typical Precipitator Ash Composition

Components	Wt%	Form of K
Na	30.6	
K	4.2	
SO ₄	56.8	
CO ₃	6.0	
Cl	2.0	
Others	0.4	
Total	100	
mol% Cl/(Na+K)	3.8	Non-Process element
mol% (CO ₃ +SO ₄)/(Na ₂ +K ₂)	96.2	Process element

Form of K in Typical Kraft Mills

- In green/white Liquor
 - Less than 1.5% of total K exists as non-process element and more than 98.5 % exists as process elements
- In precipitator ash
 - About than 4% of total K exists as non-process element and more than 96% exists as process elements
- As such, removing K will result in more Na makeup

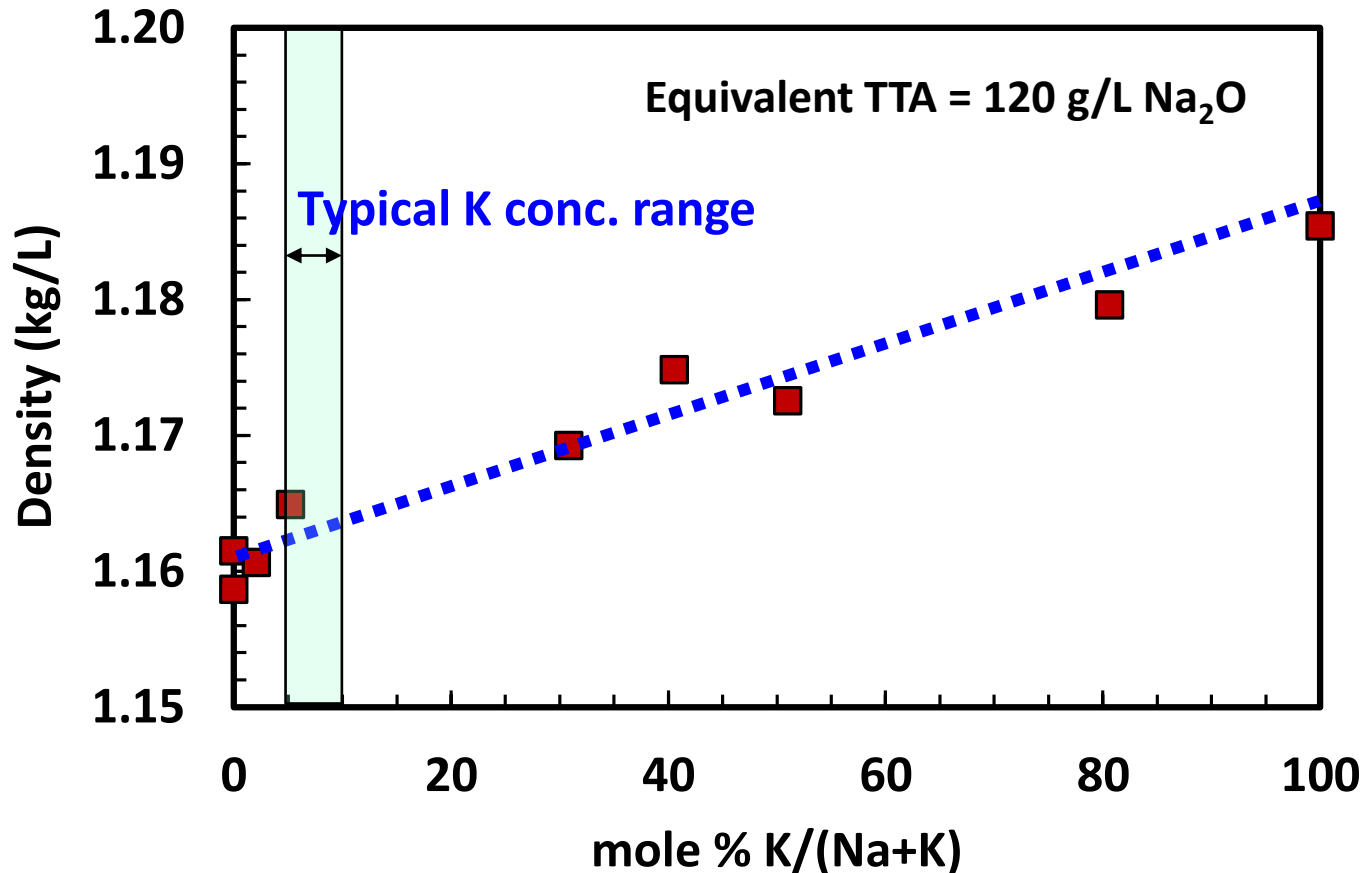
Presentation Outline

- Sources of K and Cl in kraft pulp mills
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- **Impact of K on recovery operations**
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Potassium (K) versus Sodium (Na)

- K-compounds are heavier than their Na counterparts (Atomic weight: K = 39, Na = 23)
- Per unit BLDS, increasing K results in
 - Heavier liquor
 - More ash and more smelt
 - Lower heating value
 - Higher green and white liquor density
- Since the Cl content in BLDS is about 0.5 wt% Cl and seldomly exceeds 2.5 wt% Cl and the organic content is about the same, the effect of K as NPE on all the above parameters is small.

Effect on Green Liquor Density (Na_2CO_3 - K_2CO_3 Solution)



→ *K may increase the green liquor density, but the effect is insignificant (<0.2%)*

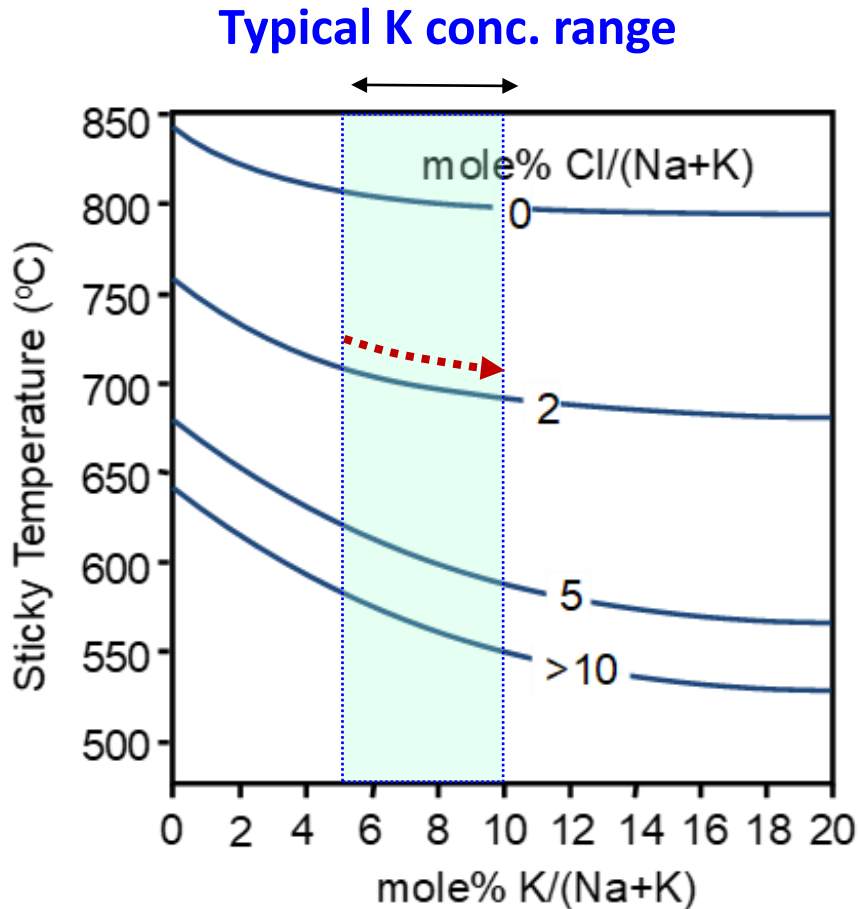
Effect on Evaporator Fouling

- Not well understood
- Soluble scale (burkeite/di-carbonate) formation
 - K content in soluble scale is slightly higher than that in black liquor → K may play a small role
- Insoluble scale (aluminosilicates) formation
 - K/Na ratio of insoluble scale is about the same as that in black liquor → K has **NO** effect

Effect on Recovery Boiler Operation

- Lowers deposit first melting temperature
 - Superheater corrosion
- Lowers deposit sticky temperature
 - Increasing fouling and plugging
- The effect increases with an increase in Cl content
 - Importance of liquid content (a function of Cl^- content, S^{2-} content, temperature)

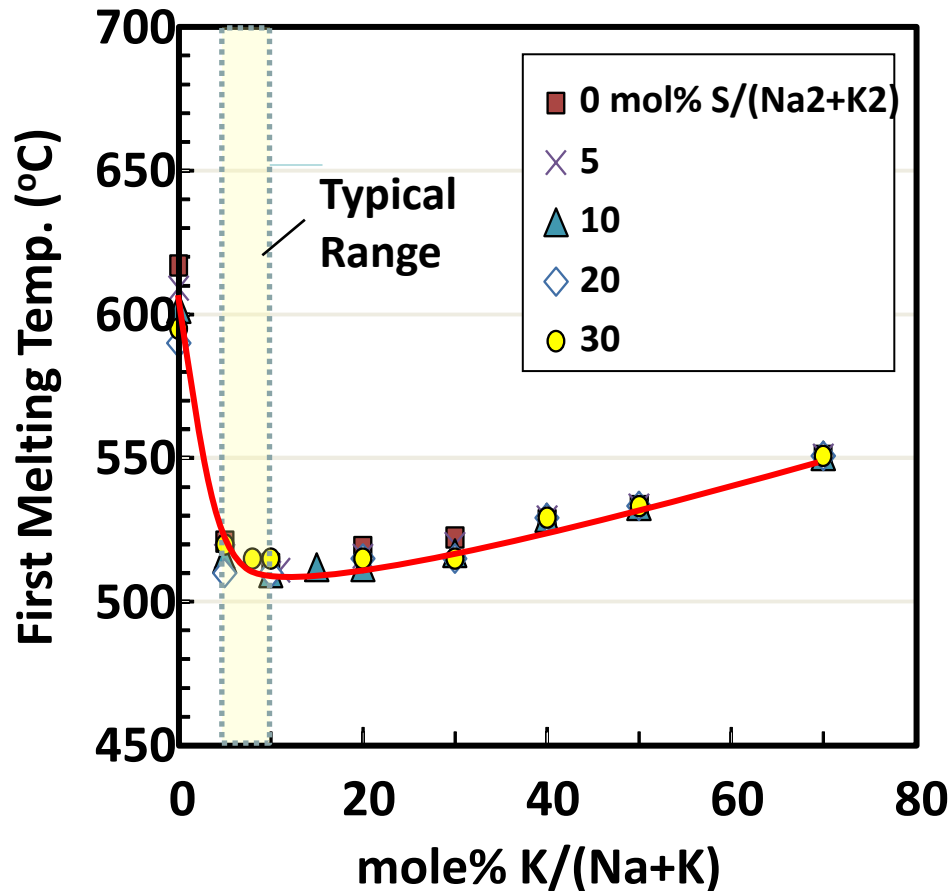
Effect on Deposit Sticky Temperature



- At a typical Cl content of 1.6 mole% Cl/(Na+K), K lowers deposit sticky temperature by 15 deg C maximum
- The effect of K is much smaller than that of Cl

Effect on First Melting Temperature

1 mol% Cl/(Na+K); 69 mol% CO₃ (Na₂+K₂)



- FMT decreases drastically to 510°C as K content increases to 5 mole% K/(Na+K).
- Above this K content, FMT increases.
- Special considerations are needed for boilers operated at $T_{\text{Steam}} > 490^{\circ}\text{C}$ to avoid SH corrosion

Effect on Scale Formation in Recausticizing Plant Equipment

	Pirssonite	Calcite
	(wt%)	(wt%)
Ca	16.0	38.3
Na	18.7	0.73
Mg	0.16	0.57
S	0.28	0.23
Mn	0.05	0.44
Fe	0.03	0.25
Al	0.03	0.07
Si	0.04	0.09
P	Trace	0.04
K	0.02	0.01
Others	0.05	0.15

- Both pirssonite and calcite scales contain very little K, <0.02 wt%.

→ *K plays no role in pirssonite/calcite scale formation*

Effect on Lime Kiln Operation

- K content in lime mud is typically very low, < 400 ppm
- Such a small amount should have no effect on kiln

Summary

- Potassium (K) has long been considered as a non-process element (NPE) in the kraft recovery process.
- This work shows clearly that it is NOT.
 - Only K bound with chloride (Cl) is NPE the rest is PE. This means that $< 2\%$ of total K is NPE.
- Since over 98% of total K is process element, removing K from the recovery cycle will require additional Na makeup to maintain the same liquor quality.

Summary

- **K has no effect on scale formation in evaporators and causticizing plant equipment, and on lime kiln operation.**
- **K may make recovery boilers more susceptible to fouling, plugging and SH corrosion, the effect, however, is much smaller than Cl.**
- **As long as the Cl content is low, K should not be a concern.**

Thank You