RECOVERY BOILER CHEMICAL PRINCIPLES

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RECOVERY BOILER CHEMICAL PRINCIPLES - OUTLINE

- **S and Na in recovery boilers - an overview**
- **Lower furnace and char bed**
- **Flue gases and dust**
- **Foreign components**

KRAFT BLACK LIQUOR ELEMENTARY COMPOSITION

(Sample before the mixing tank)

C	**38.2**	**% in BL dry solids**
H	**3.4**	
O	**31.1**	
N	**0.1**	
S	**5.2**	
Na	**19.8**	
K	**1.9**	
Cl	**0.1**	
Others (Ca,Si,Fe,Mg,Al,Mn)	**0.2**	

$S/Na_2 = 0.38$

SULPHUR COMPOUNDS IN KRAFT BLACK LIQUORS

(Sample before the mixing tank)

Sulphide, S^{2-}	**11 %**	**S of total S**
Thiosulphate, $S_2O_3^{2-}$	**36 %**	
Sulphite, SO_3^{2-}	**13 %**	
Sulphate, SO_4^{2-}	**5 %**	
Organic S (balance)	**35 %**	
	100 %	

Na AND S COMPOUNDS IN RECOVERY FURNACE

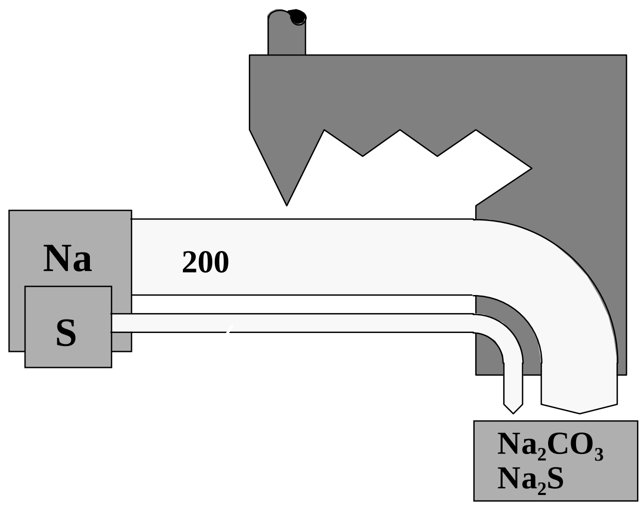
Solids or liquids	Gases
Na_2S	H_2S (g)
Na_2CO_3	SO_2 (g)
Na_2SO_4	
NaOH	NaOH (g)
$NaHSO_4$	

Na AND S COMPOUNDS IN RECOVERY FURNACE

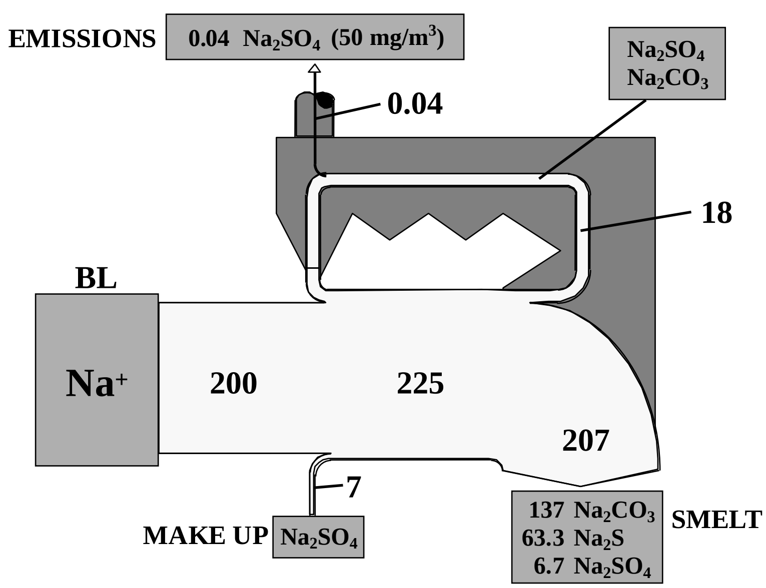
Solids or liquids		Gases
Na_2S	mp 1180°C/2160 F	H_2S (g)
Na_2CO_3	mp 860°C/1580 F	SO_2 (g)
Na_2SO_4	mp 880°C/1620 F	
NaOH	mp 320°C/610 F	NaOH (g)
$NaHSO_4$	mp 180°C/360 F	

RECOVERY FURNACE CHEMISTRY

(g sulphur/kg BL solids)



SODIUM BALANCE IN A KRAFT RECOVERY BOILER (g Na/kg BL solids)



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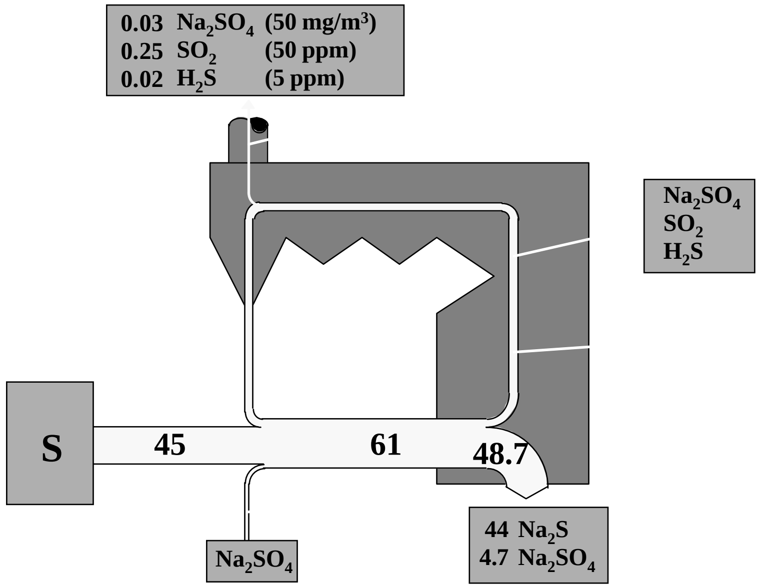

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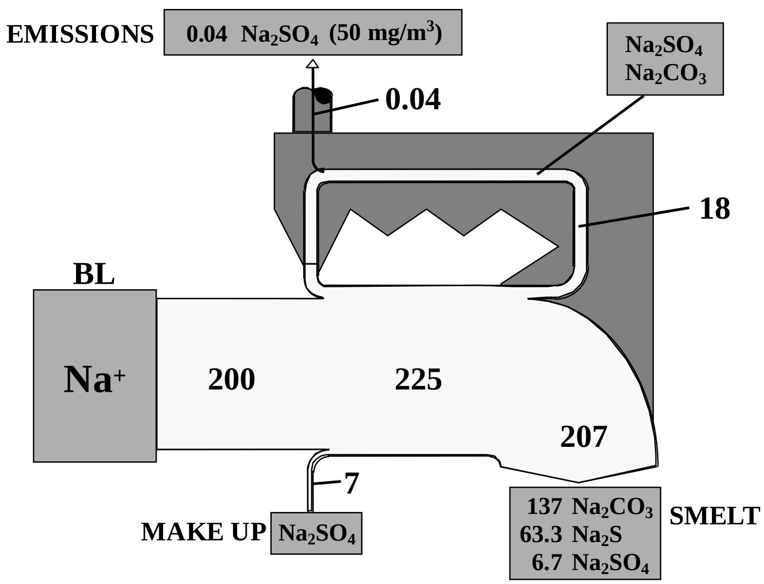


SULPHATE REDUCTION IN SMELT

- **Either:**

$$Na_2SO_4 \xrightarrow{CO,\ H_2} Na_2S$$

- **Or:**

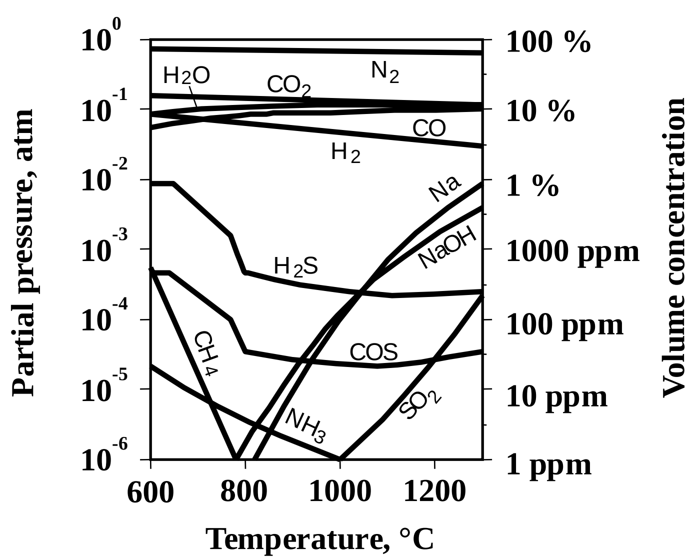
$$Na_2SO_4 \xrightarrow{C_{solid}\ (char)} Na_2S$$

SULPHATE REDUCTION - SUMMARY

- **Sufficient amount of char in the bed**
- **High enough temperature**

  (T = +50°C doubles the rate)

EQUILIBRIUM COMPOSITION OF LOWER FURNACE GASES VS. TEMPERATURE



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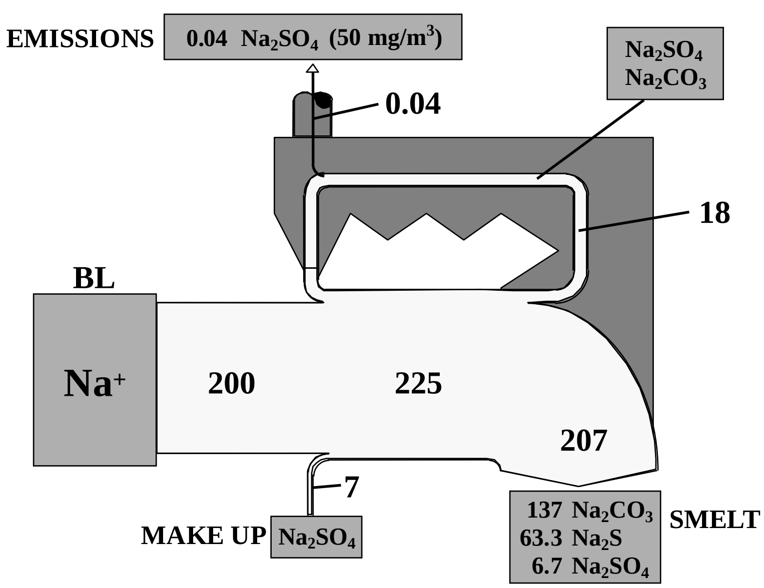
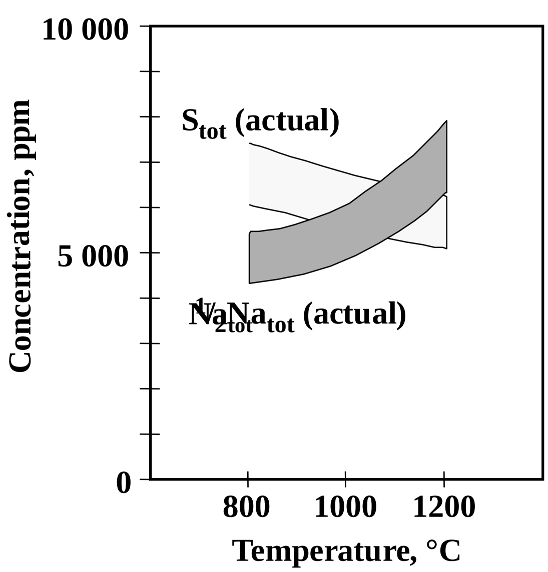


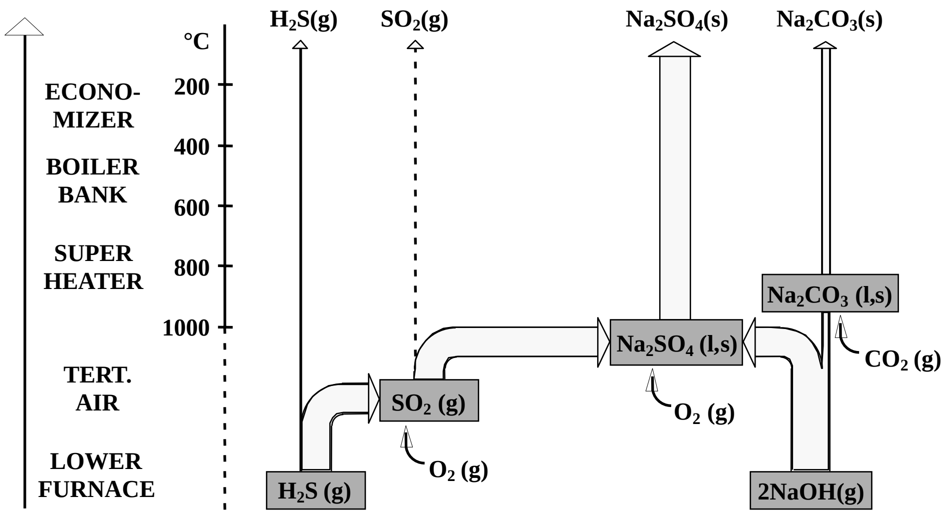
RELEASE OF S AND Na IN LOWER FURNACE

- Mainly H_2S and NaOH
- At increasing temperature:
  S release decreases
  Na release increases
- $(S/Na_2)_{flue\ gases}$ = 0.8 - 1.5

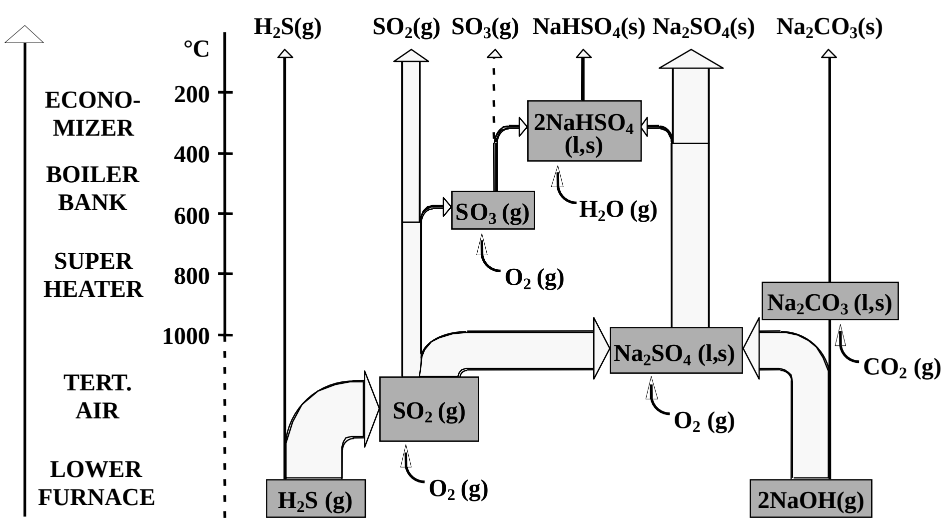
RECOVERY FURNACE GASEOUS SULFUR AND SODIUM – TYPICAL DATA



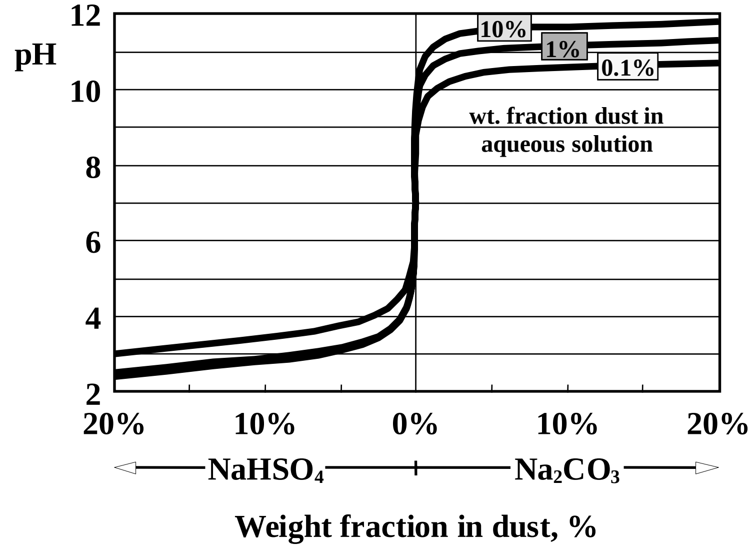
REACTIONS OF S AND Na IN FLUE GASES
(S/Na_2 = 0.8, hot bed, low sulphidity)



REACTIONS OF S AND Na IN FLUE GASES
(S/Na_2 = 1.5, cool bed, high sulphidity)

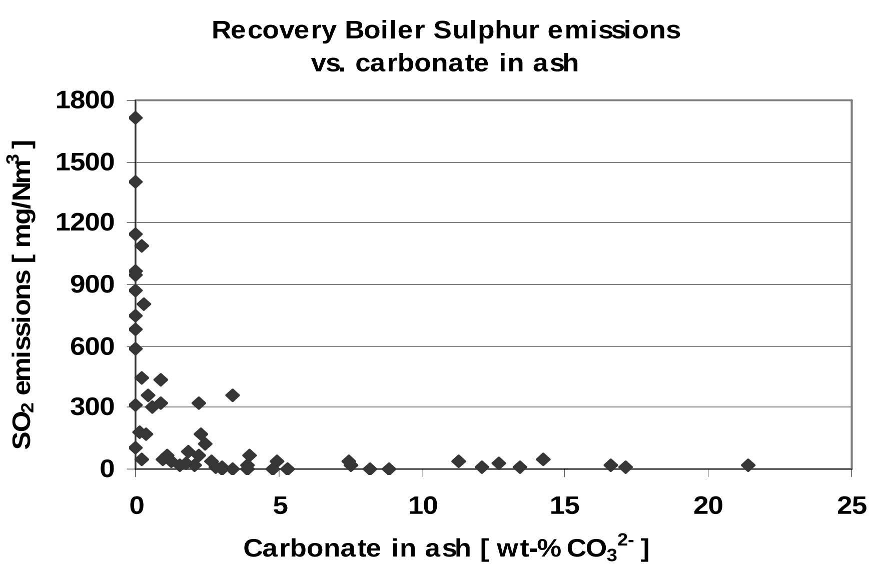


DUST pH vs. DUST COMPOSITION



SO2 vs CARBONATE IN DUST

(Courtesy Kvaerner Pulping 2002)



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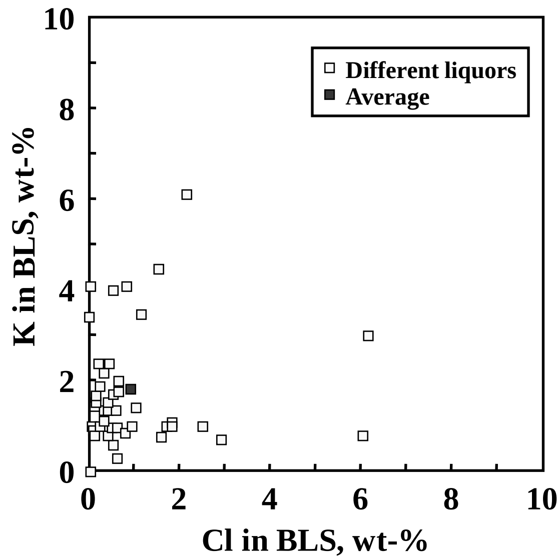
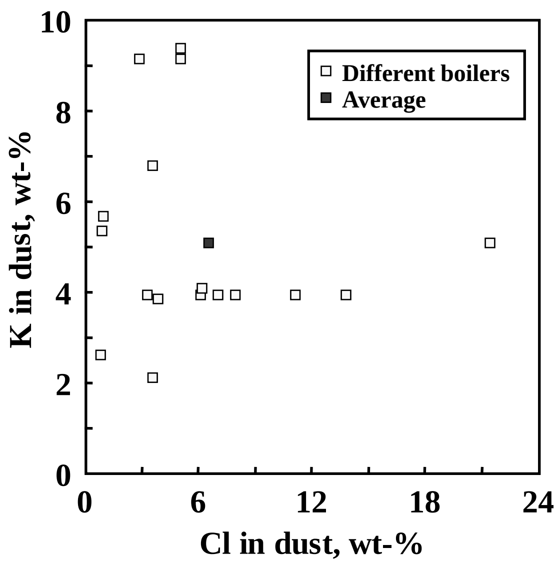
K AND Cl IN NORTH AMERICAN BLACK LIQUORS



K AND Cl IN PRECIPITATOR DUST



POTASSIUM AND CHLORINE IN LOWER FURNACE

- **Enrichment factors:**

$$\left.\begin{array}{l}\dfrac{(Cl/Na)\text{ in gas}}{(Cl/Na)\text{ in smelt}}\\[2em]\dfrac{(K/Na)\text{ in gas}}{(K/Na)\text{ in smelt}}\end{array}\right\}\ -\ 2...4$$

POTASSIUM AND CHLORINE IN LOWER FURNACE

- Mainly NaCl
  KCl
  KOH

POTASSIUM AND CHLORINE CHANGE MELTING OF Na SALTS

- Smelt freezing point decreases (typically 850 C --> 700 C)
- Dust particle sticky temperatures decrease (800 C --> 600 C)

FOREIGN COMPONENTS SUMMARY (I)

- Cl and K are enriched in gas phase
- Lower furnace: NaCl, KCl, KOH

FOREIGN COMPONENTS SUMMARY (II)

- K and Cl make dust more "sticky"
- If $(S/Na_2)_{FG}$ high enough:

$$NaCl \xrightarrow{SO_2/O_2} Na_2SO_4$$

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- **Conclusions**

RB CHEMISTRY - CONCLUSIONS (I)

- **Good reduction requires:**
  - **- char in the bed**
  - **- high enough temperature**

RB CHEMISTRY - CONCLUSIONS (II)

- **Dust/flue gas chemistry controlled by S/Na_2 ratio in flue gas**
- **Flue gas S/Na_2 ratio decreases when:**
  - furnace temperature increases
  - liquor sulphidity decreases

RB CHEMISTRY - CONCLUSIONS (III)

- **Low S/Na_2 gives low SO_2 emissions and alkaline dust (Na_2CO_3)**
- **High S/Na_2 gives high SO_2 emissions and acidic dust ($NaHSO_4$)**
- **Dust pH good indicator**

RB CHEMISTRY - CONCLUSIONS (IV)

- **K and Cl are enriched in the flue gases**
- **K and Cl in the dust lower melting temperature range**
- **At high S/Na_2 chlorine is released from the dust ($NaCl \rightarrow HCl$)**