

# Modelling the super-equilibrium of sodium, potassium, sulphur and chlorine in the recovery boiler fume

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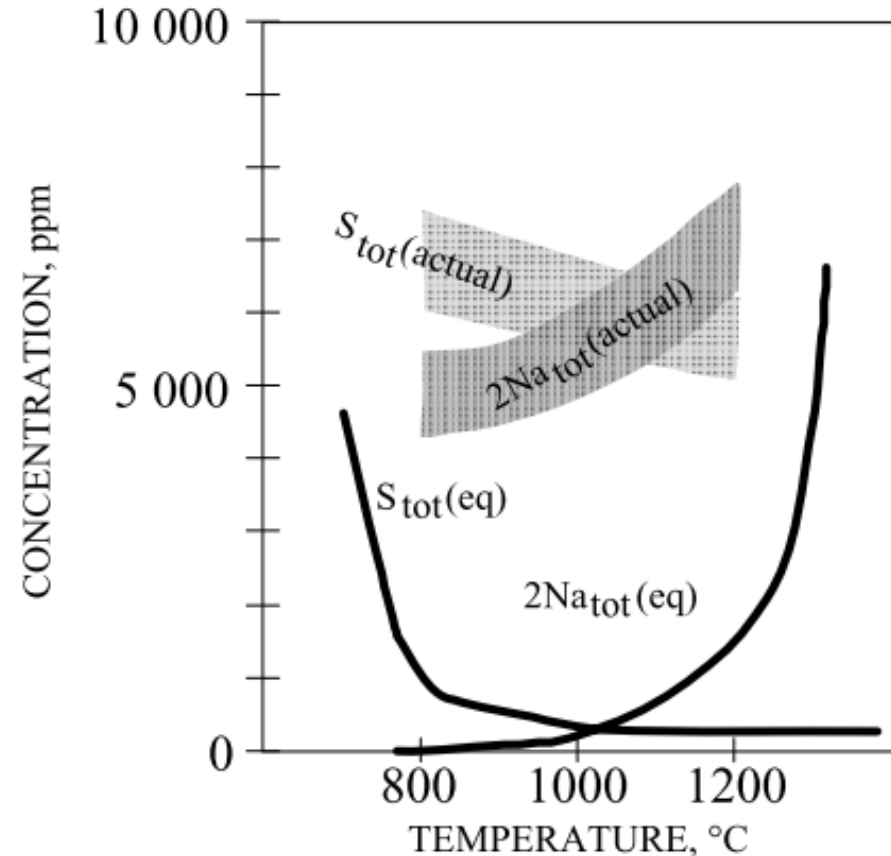
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[1] Kangas P, Koukkari P, Lindberg D, Hupa M. Modelling black liquor combustion with the constrained Gibbs energy method. 8th International Black Liquor Colloquium, Belo Horizonte, Brazil: 2013.

[2] Kangas P, Koukkari P, Lindberg D, Hupa M. Modelling black liquor combustion with the constrained Gibbs energy method (submitted). The Journal of Science and Technology for Forest Products and Processes 2013.

# Background

- Black liquor combustion [1] in recovery boiler and black liquor gasification [2,3] and related chemistry are modelled by thermodynamic equilibrium based on the Gibbs' energy minimisation.
- It is known that the sodium and sulphur concentrations in the fume of industrial processes differ from the modelled concentrations [4] (Fig. 1). Also potassium and chlorine are enriching to the fume.
- Super-equilibrium is formed.
- A proposed explanations of the phenomena is very rapid, kinetically constrained pyrolysis of droplets at the earlier stage of combustion. [4]



**Table 1.** Release of sulphur, sodium, potassium and chloride to flue gases

	S	Na	K	Cl	Type
Hupa et al. [5]	54 %	17 %			Laboratory
Salmenoja et al. [6]			1.1-1.4	1.0-6.0	Industry
Mikkanen et al. [7]	24-36 %	10-12%	1.3-1.7		Industry
Janka et. al [8]			1.3-1.6	3.0-4.5	Industry
Vakkilainen [9]			1.0-2.5	0.3-6.0	Industry

S:  $S_{\text{flue gas}}/S_{\text{black liquor}}$

Na:  $S_{\text{flue gas}}/S_{\text{black liquor}}$

K:  $(K_{\text{flue gas}}/(K + Na)_{\text{flue gas}})/(K_{\text{black liquor}}/(K + Na)_{\text{black liquor}})$ ;

Cl:  $(Cl_{\text{flue gas}}/(K + Na)_{\text{flue gas}})/(Cl_{\text{black liquor}}/(K + Na)_{\text{black liquor}})$

**Figure 1.** S and Na concentrations in the fume of recovery boiler as a function of temperature. Estimated values based on the thermodynamic equilibrium and typical industrial values [1].

## Definitions of super-equilibrium

- A state where excess amount of species occurs in particular phase compared to equilibrium state.
- A local equilibrium state with higher free energy of system.
- Only partly constrained system with additional degrees of freedom
- Examples: (i) Sorption of alkali metals to fibres, (ii) volatilisation of sodium and sulphur in recovery boilers, and (iii) formation of char, hydrocarbons, tar and ammoniac in gasification

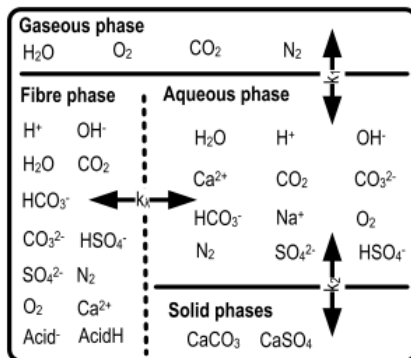


Figure i. Super-equilibrium of alkali metals in fibres (sorption) in pulp and paper mills. Constraints are electroneutrality of both aqueous phases and fibre bound acidic groups. [24]

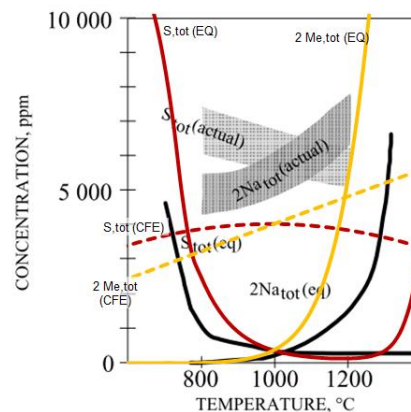


Figure ii. Super-equilibrium of volatile alkali metals and sulphur in black liquor combustion. Constraints are volatilisation and enrichment of species. [25]

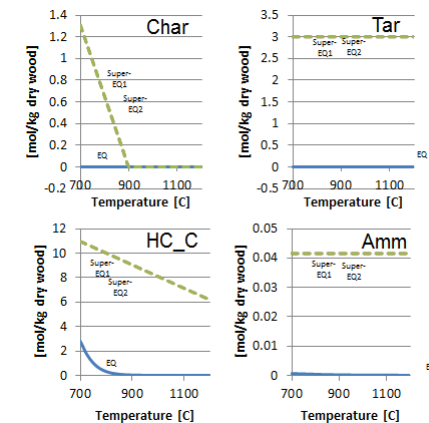


Figure iii. Super-equilibrium of char, hydrocarbons, tar and ammoniac in syngas. Constraints due to the kinetic constraints in gasification. [26]

# Background – recovery boiler modelling

- Ash chemistry (e.g. Lindberg [10]) -> Focus on phase diagrams and prediction of sticky temperatures
- Expert systems for recovery boiler (e.g. Backman et al. [11]) -> Lower furnace as boundary condition with dual approach
- Large scale process simulation (e.g. Uloth et al. [12]) -> Flue gas channel
- Droplet modelling (e.g. Järvinen et al. [13]) -> dynamic phenomena of droplets
- Fly ash particle formation (e.g. Mikkanen [14]) -> Agglomeration at the upper furnace
- Bed modelling (e.g. Engblom [15]) -> Kinetics of bed modelling, focus on carbon reactions
- CFD (e.g. Grace et al. [16] and Leppänen et al. [17]) -> Gas phase and agglomeration

**=> Apparent need for a unified model which could be used for simultaneous estimation of the chemical reactions and heat generation of lower furnace**

# Hypothesis

1. Constrained Free Energy (CFE) method can be used to predict the Na, K, S and Cl content in fume with greater detail than traditional equilibrium (EQ) calculation.
2. There is significant difference on the fume and smelt composition as well as the condensed phases of flue gas when CFE method is applied.
3. A better prediction of Na, K, S and Cl in the fume could improve the computational analysis of boiler problems.

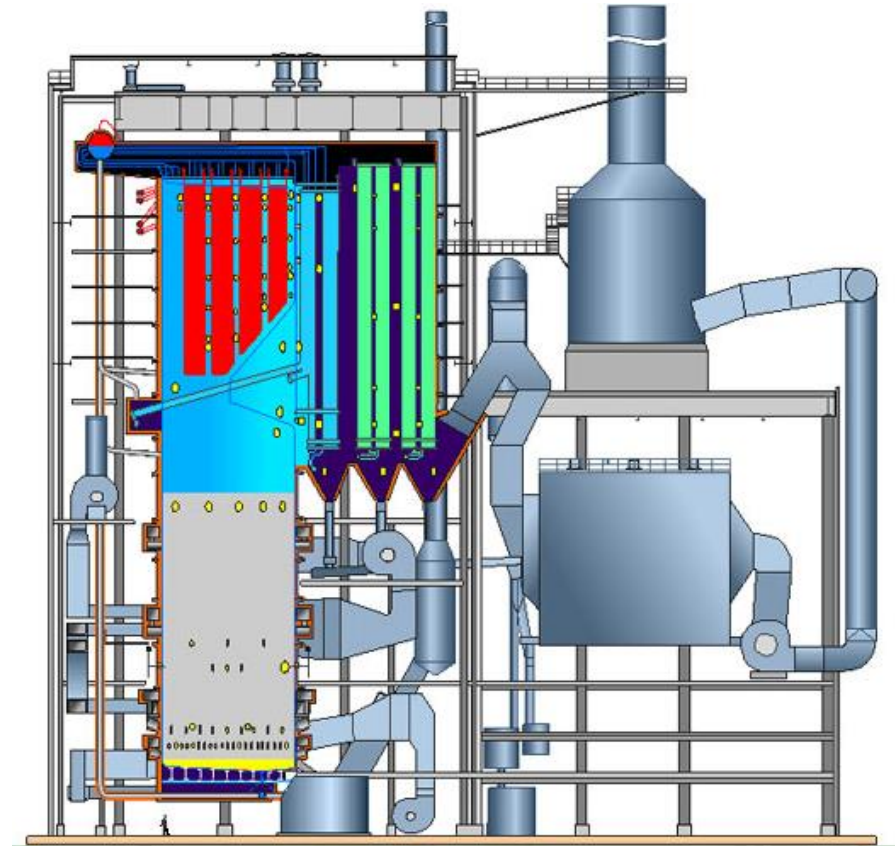


Figure 2. An example of recovery boiler [18].

# Methodology

- Modelling the recovery boiler combustion process is done in two parts: (i) lower part of the furnace and (ii) upper part and flue gas channel.
- Oxygen demand in combustion is calculated according [3]. Only fume is considered. (Carry-over is not included).
- BL composition is shown in Table 2.
- BL is described based on the elements and HHV of black liquor.

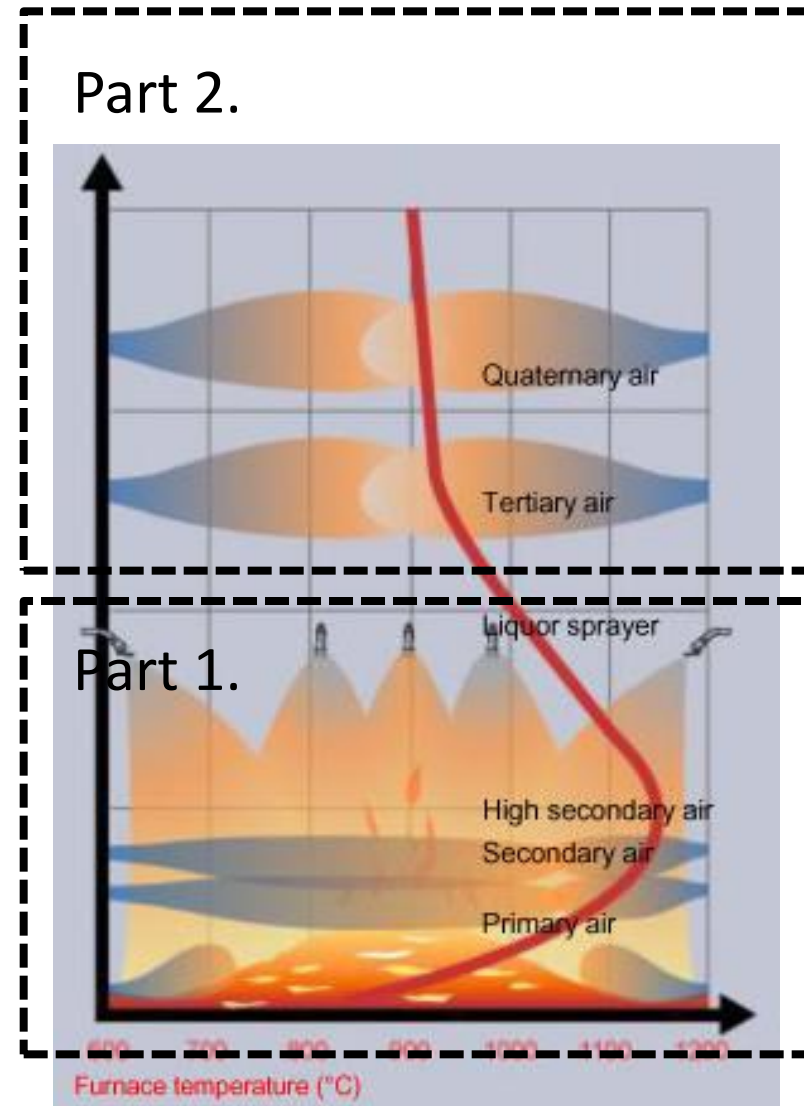
**Table 2.** Black liquor composition used in this study [4]

C	H	Na	K	S	Cl	N	O	Moisture content	S/2Me -ratio
[wt-%]	[wt-%]	[wt-%]	[wt-%]	[wt-%]	[wt-%]	[wt-%]	[wt-%]	[wt-%]	[%]
32.3	3.3	21.4	2.3	5	0.7	0.1	34.9	20	31.5

# Methodology

## Model definition

- Part 1 of model
  - Lower part of furnace
  - Liquor spraying, drying, pyrolysis, char combustion, reactions in char bed
  - Black liquor and air as input streams
  - Air:  $\lambda_{\text{furnace}} = 0.7$ ,
  - Temperature range 600 – 1400 C
  - Both equilibrium (EQ) and constrained equilibrium (CFE) are studied in part 1
- Part 2 of model
  - Upper furnace
  - Flue gas channel, heat exchangers
  - Two cases (cold furnace: 900 C and hot furnace: 1100 C) are calculated
  - Gas phase from part 1 and air are used as input streams
  - Excess air
  - Temperature range 1200 -> 200 C
  - Only equilibrium (EQ) is considered



**Figure 3.** Two parts of the developed model . Background figure from [18].

# Methodology

## Constrained Free Energy (CFE)

- Use of immaterial constraints in Gibbs energy minimization was first introduced by Alberty [27] and further developed for reaction kinetics by Keck and Koukkari [28,29] and further defined as Constrained thermodynamic equilibria (CFE) technique and applied for various applications by Koukkari and Pajarre [22,23].
- Commercial minimisation software ChemSheet [20] is applied.
- A typical chemical system (Na-K-S-Cl-C-O-H-N) for black liquor combustion is obtained from [21]. System is described in more detail in [10].
- Gibbs' free energy method is extended with additional virtual constraints.
- Extended model is used to predict the super-equilibrium of Na, K, S and Cl in fume.
- Constraints:
  - Na in the fume: 10 % total Na at 1000 C
  - S in the fume: 30.0 % of total S at 1000 C ( $S/2Me = 1$  at 1000C)
- Enrichment factors:
  - K in the fume:  $EF_K = 1.4$
  - Cl in the fume:  $EF_{Cl} = 2.5$



# Methodology - Constrained Free Energy

**Table 3.** Sample of the extended stoichiometric matrix. Original database is from (FactSage 2013). Four virtual system components (Na\*, S\*, K\* and Cl\*) and four virtual constituents (R\_Na, R\_K, R\_S, R\_Cl) are introduced for calculation of super-equilibrium.

Phase	Constituent	K	Cl	S	Na	O	N	C	H	Na*	K*	S*	Cl*
Gas phase	H								1				
	Na				1					1			
	NaOH				1	1			1	1			
	H2O					1			2				
	CO					1		1					
	NaCl		1		1					1			1
	KCl	1	1								1		1
	SO <sub>2</sub>			1		2						1	
...	...												
ASalt-liquid	Na <sub>2</sub> CO <sub>3</sub>				2	3		1					
C	C							1					
...	...												
R_Na	R_Na									+1			
R_K	R_K										+1		
R_S	R_S											+1	
R_Cl	R_Cl												+1

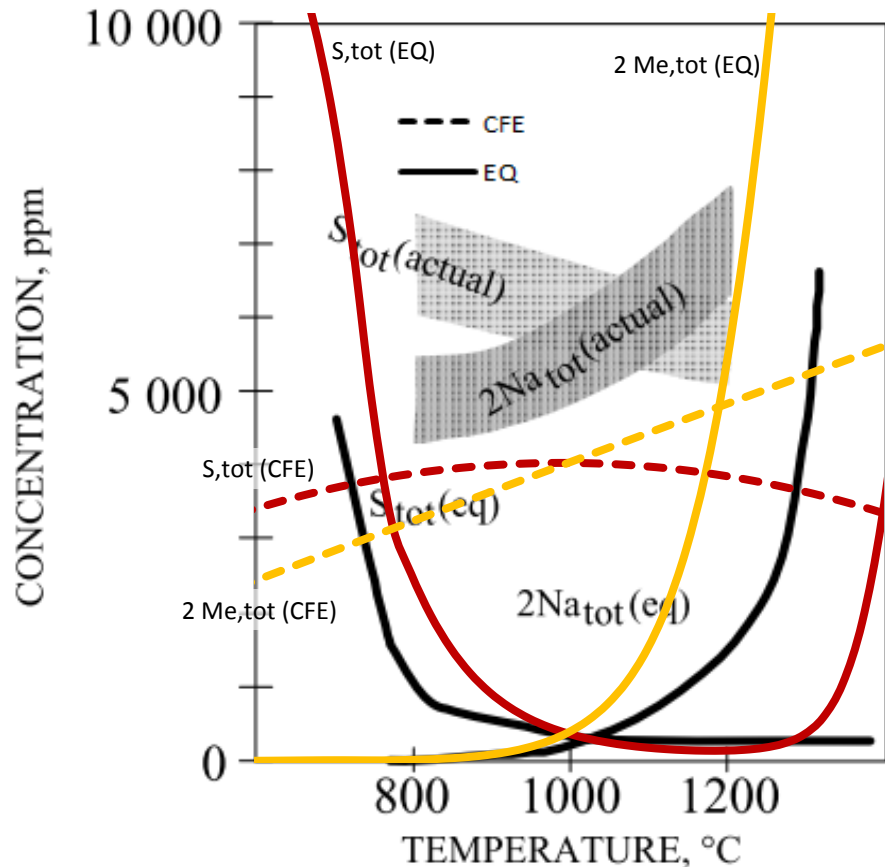
## Constrained equilibrium

- From solid to gas
- $\text{Na}_2\text{CO}_3(\text{s}) + 2\text{C}(\text{s}) \rightarrow 2\text{Na}(\text{g}) + 3\text{CO}(\text{g})$
- $\Delta_r G \neq 0$
- E.g. 
$$\begin{aligned} \text{Aff} &= -\Delta_r G = \mu_{\text{Na}_2\text{CO}_3} + \mu_{2\text{C}} - (\mu_{2\text{Na}} + \mu_{3\text{CO}}) \\ &= 2\pi_{\text{Na}} + \pi_{\text{C}} + 3\pi_{\text{O}} + 2\pi_{\text{C}} - (2\pi_{\text{Na}} + 2\pi_{\text{Na}^*} + 3\pi_{\text{C}} + 3\pi_{\text{O}}) \\ &= -2\pi_{\text{Na}^*} \neq 0 \end{aligned}$$

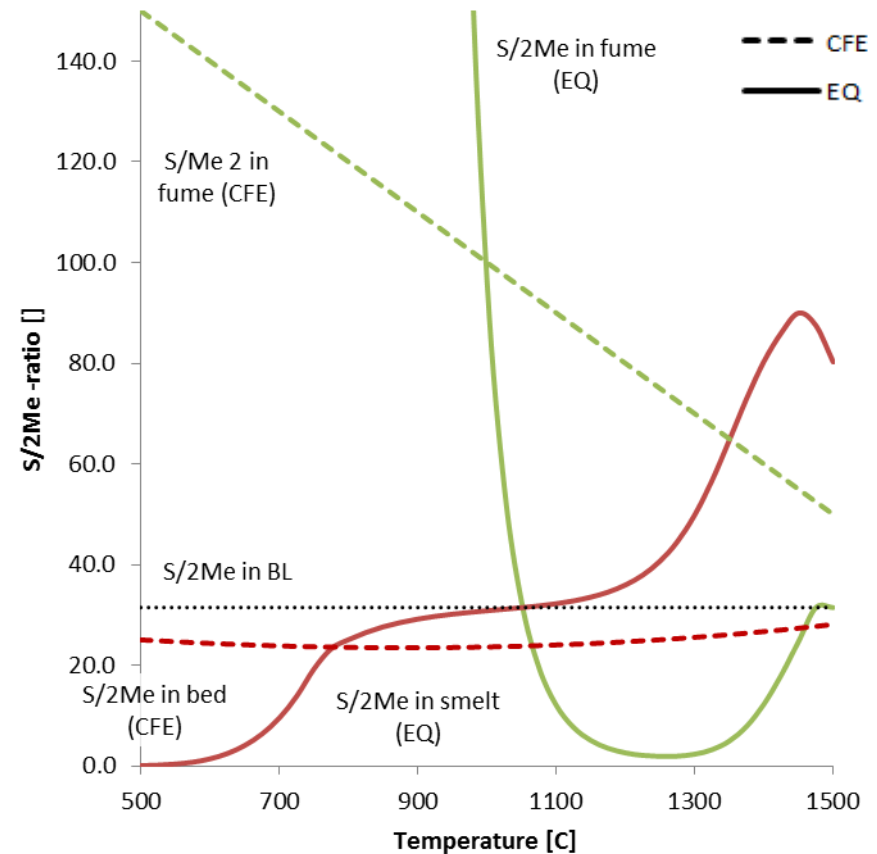
## Thermodynamic equilibrium

- Reactions in gas
- $\text{Na}^+(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{NaOH}(\text{g}) + \text{H}^+(\text{g})$
- $\Delta_r G = 0$
- E.g. 
$$\begin{aligned} \text{Aff} &= -\Delta_r G = \mu_{\text{NaOH}} + \mu_{\text{H}} - (\mu_{\text{Na}} + \mu_{\text{H}_2\text{O}}) \\ &= \pi_{\text{Na}} + \pi_{\text{O}} + \pi_{\text{H}} + \pi_{\text{Na}^*} + \pi_{\text{H}} - (\pi_{\text{Na}} + \pi_{\text{Na}^*} + 2\pi_{\text{H}} + \pi_{\text{O}}) \\ &= 0 \end{aligned}$$

# Results – Model vs. reference

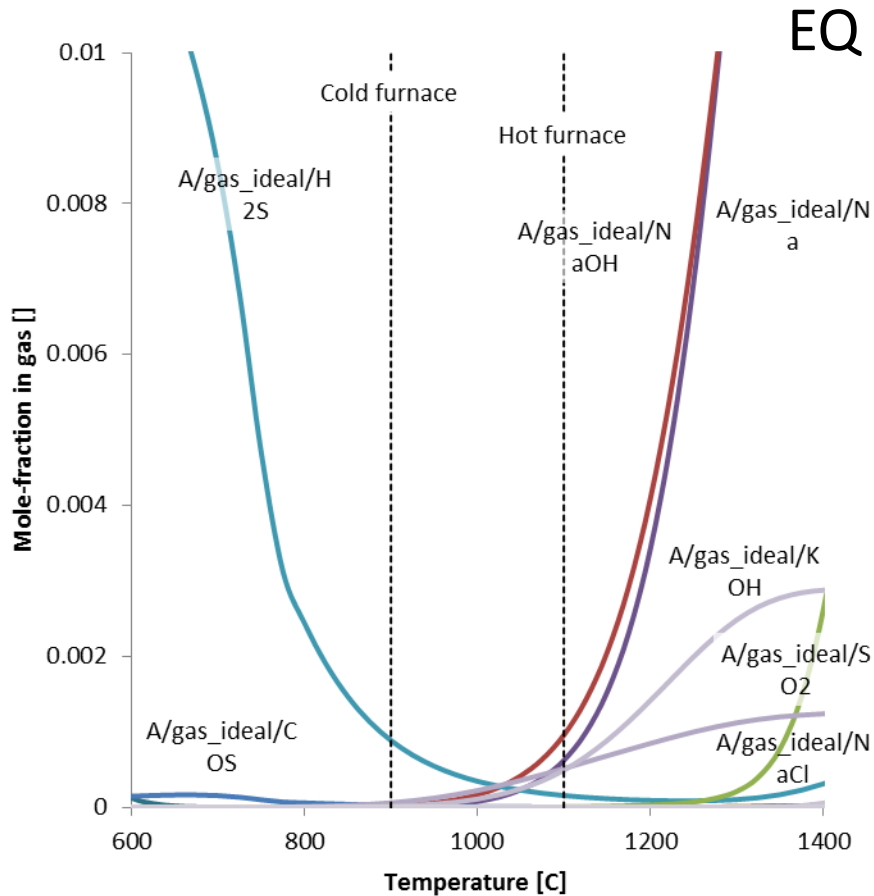


**Figure 4.** Equilibrium concentrations of S and 2 Me (2 Na + 2 K) in the fume of recovery boiler as a function of temperature.  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10\%$ ,  $x_{\text{S}} = 30\%$  at 1000 C.  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$ . Reference figure from [1].

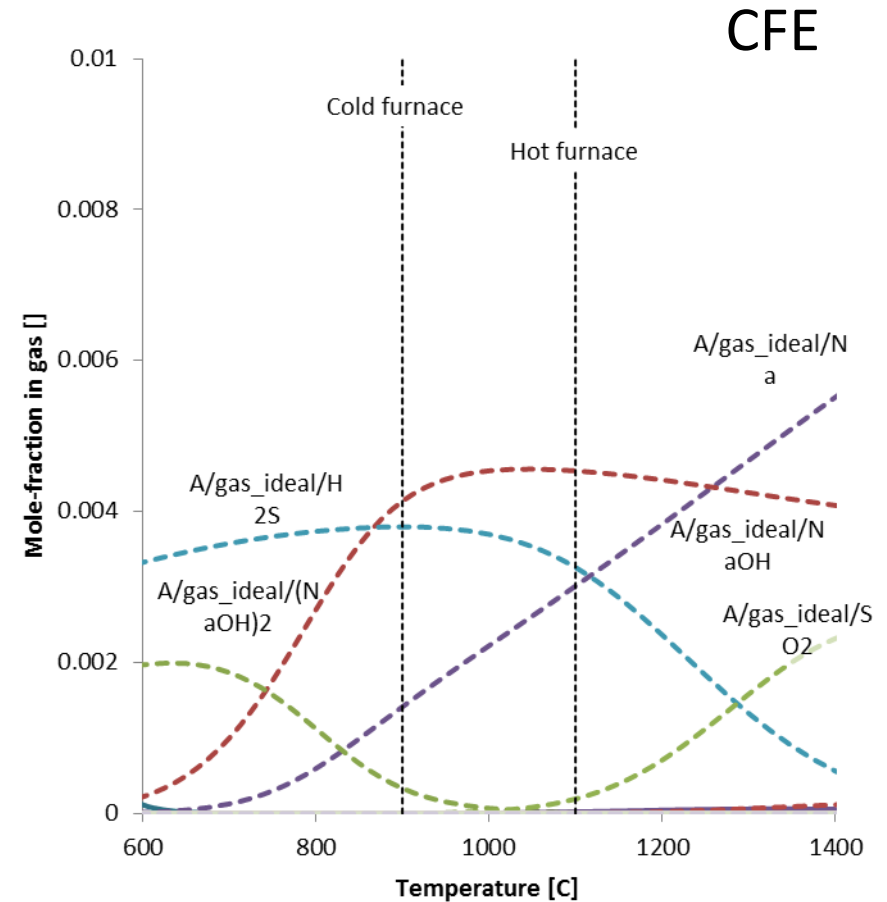


**Figure 5.** S/2Me - molar-ratio of fume, smelt and black liquor. Dashed lines refer to CFE, solid lines to EQ.  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10\%$ ,  $x_{\text{S}} = 30\%$  at 1000 C.  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$ .

# Results – Na and S in the fume



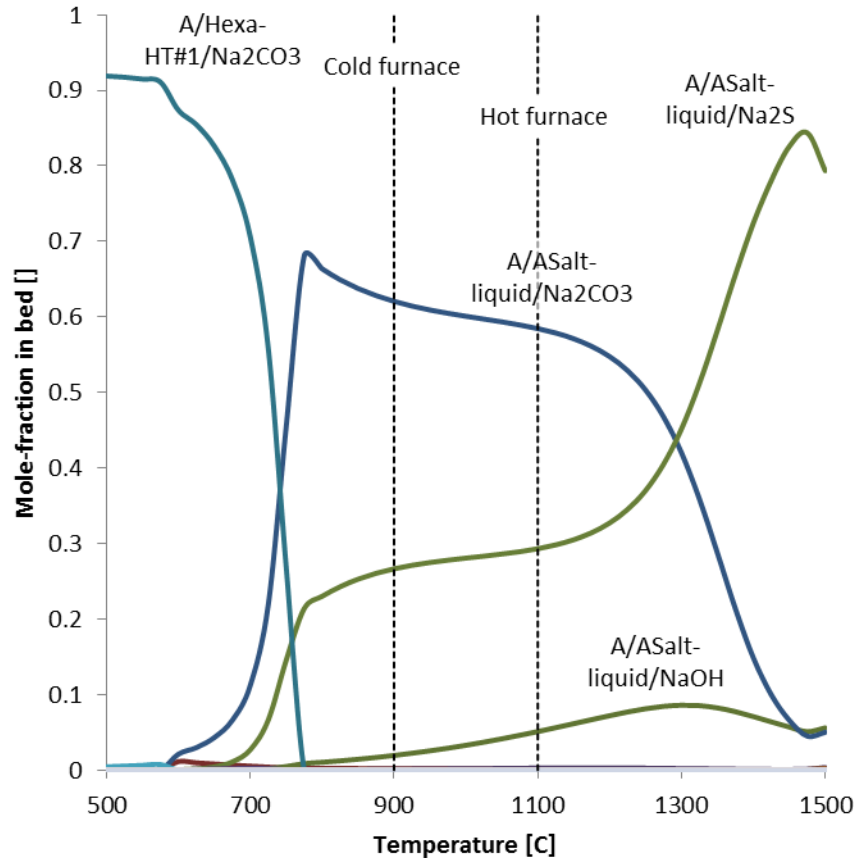
**Figure 6.** Equilibrium concentrations of S and Na in the fume. Only major constituents including S and Na shown.  $\lambda_{furnace} = 0.7$ . Volatility:  $x_{Na} = 10\%$ ,  $x_S = 30\%$  at 1000 C.  $EF_K = 1.4$  and  $EF_{Cl} = 2.5$ .



**Figure 7.** Constrained equilibrium concentrations of S and Na in the fume. Only constituents including S and Na shown.  $\lambda_{furnace} = 0.7$ . Volatility:  $x_{Na} = 10\%$ ,  $x_S = 30\%$  at 1000 C.  $EF_K = 1.4$  and  $EF_{Cl} = 2.5$ .

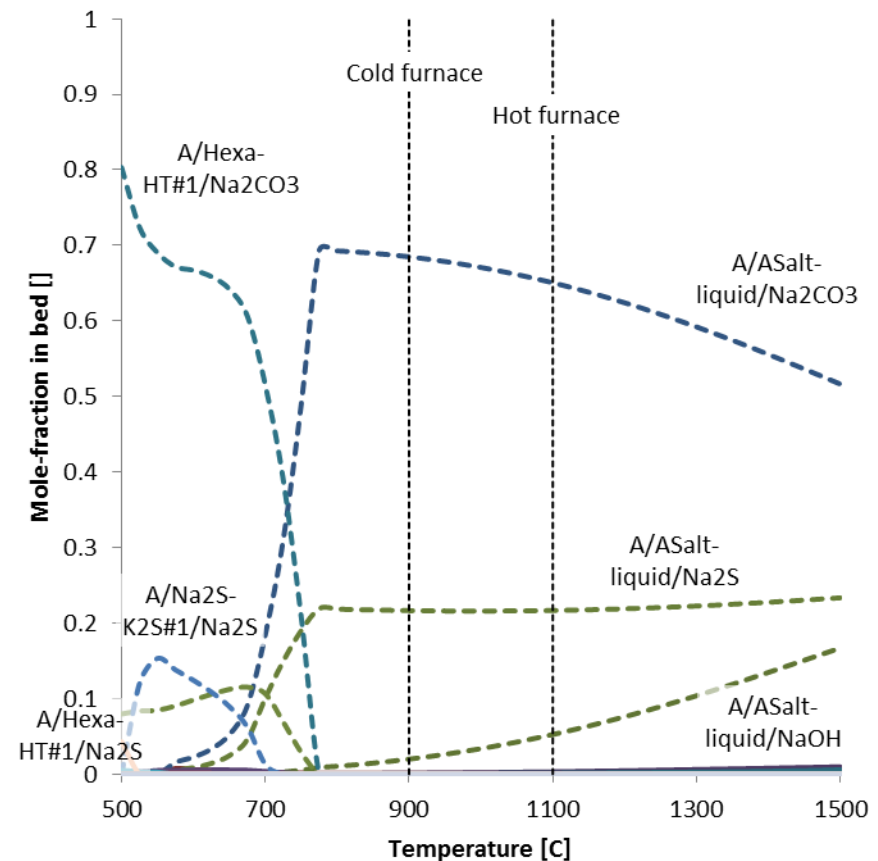
# Results – Na and S in smelt

EQ



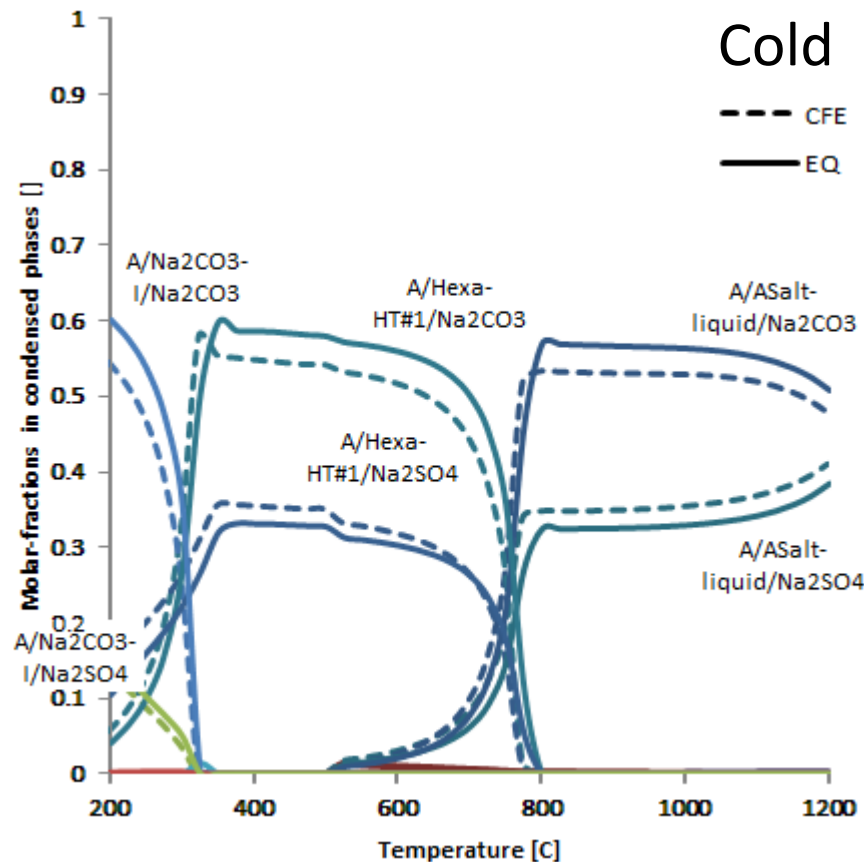
**Figure 8.** Equilibrium concentrations of S and Na in smelt. Only major constituents shown.  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10\%$ ,  $x_{\text{S}} = 30\%$  at 1000 C.  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$ .

CFE

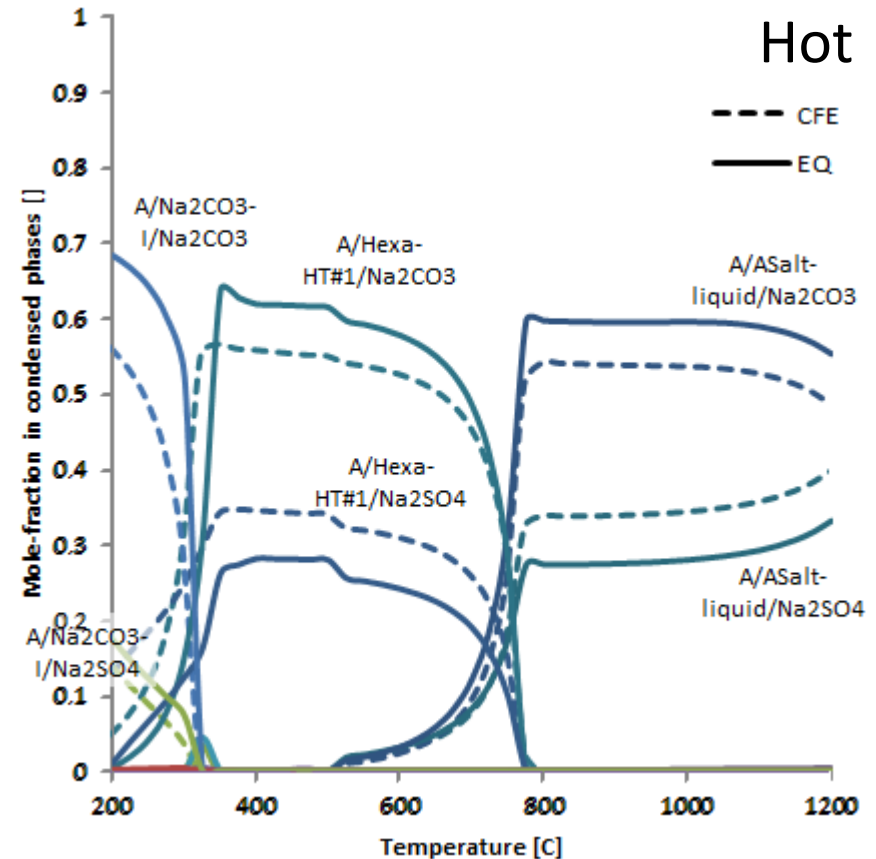


**Figure 9.** Constrained equilibrium concentrations of S and Na in smelt. Only major constituents shown.  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10\%$ ,  $x_{\text{S}} = 30\%$  at 1000 C.  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$ .

# Results – Na and S in condensed phases from the fume

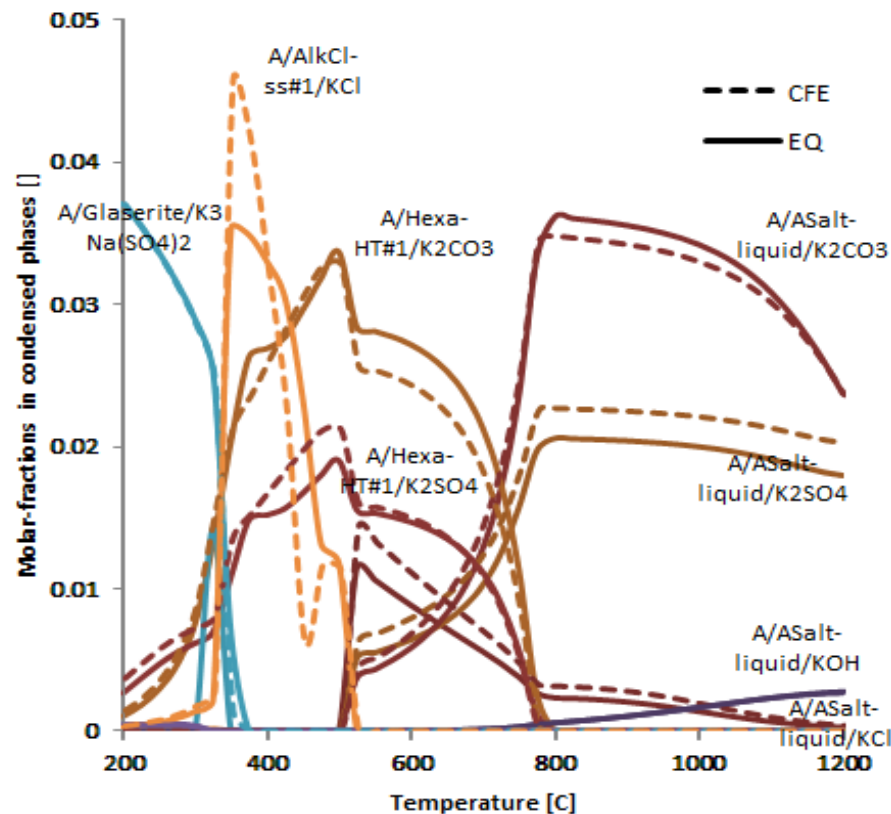


**Figure 11.** Condensed phases from the fume Only major constituents shown. Dashed lines refer to CFE, solid lines to EQ.  $T_{\text{furnace}} = 900$  C.  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10$  %,  $x_{\text{S}} = 30$  % at 1000 C.  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$ .

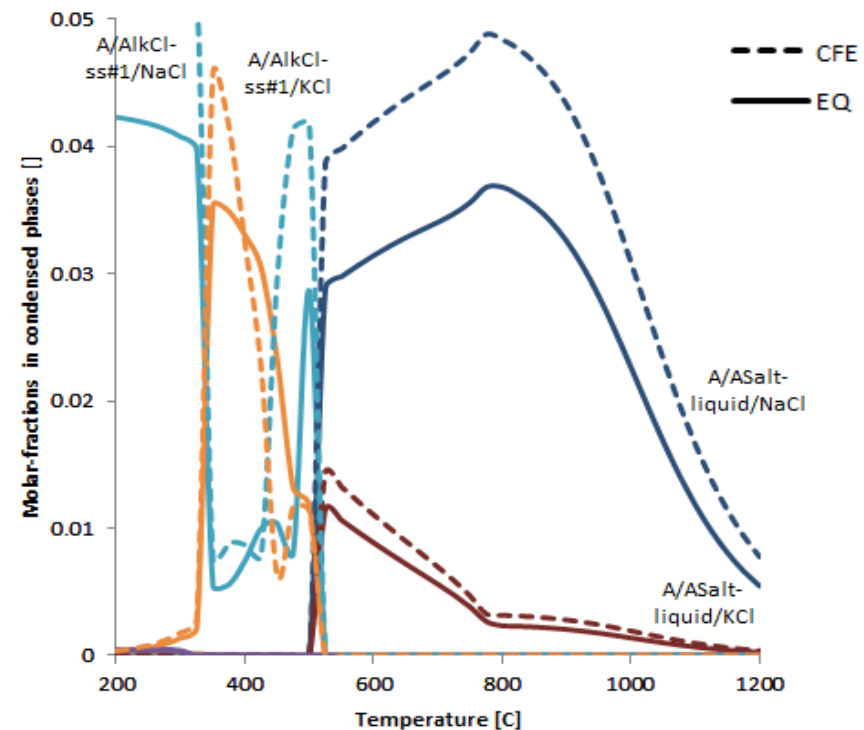


**Figure 12.** Condensed phases from the fume Only major constituents shown. Dashed lines refer to CFE, solid lines to EQ.  $T_{\text{furnace}} = 1100$  C.  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10$  %,  $x_{\text{S}} = 30$  % at 1000 C.  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$ .

# Results –K and Cl in condensed phases from the fume

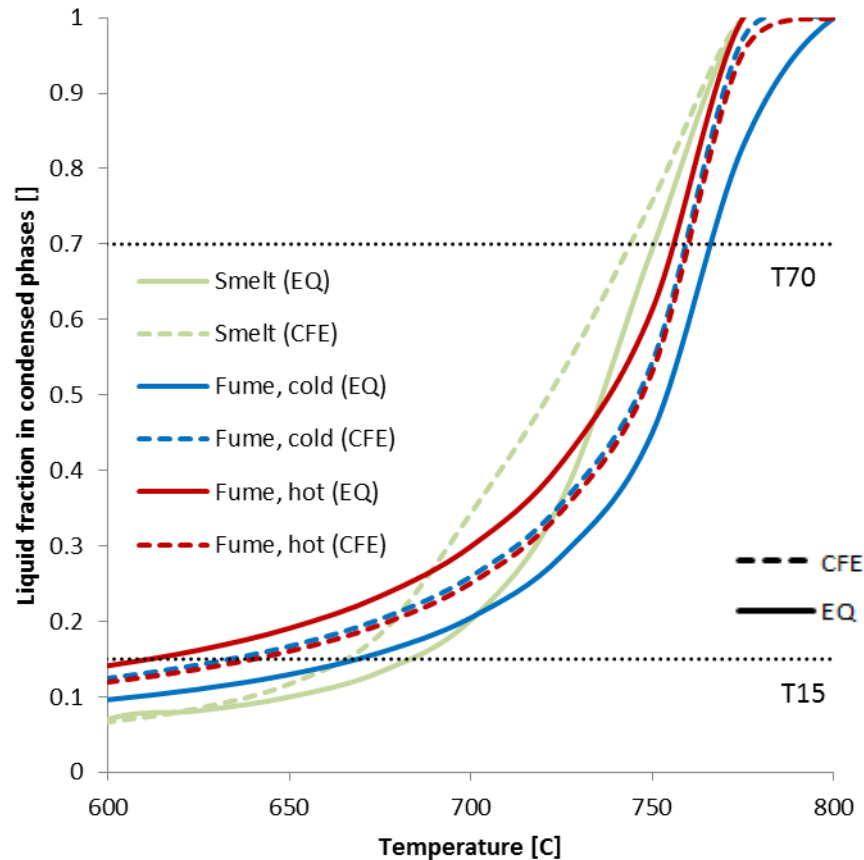


**Figure 13.** Condensed phases from the fume. Major constituents with potassium shown. Dashed lines refer to Super-EQ, solid lines to EQ.  $T_{\text{furnace}} = 900 \text{ C}$ .  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10 \%$ ,  $x_{\text{S}} = 30 \%$  at  $1000 \text{ C}$ .  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$

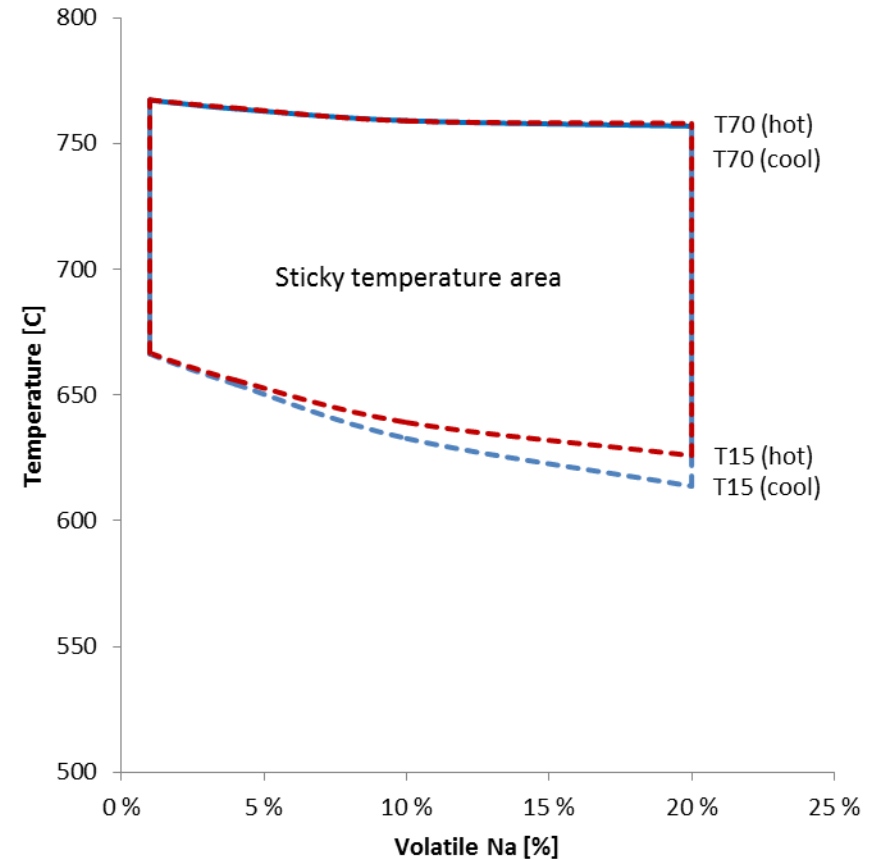


**Figure 14.** Condensed phases from the fume. Major constituents with chlorine shown. Dashed lines refer to Super-EQ, solid lines to EQ.  $T_{\text{furnace}} = 900 \text{ C}$ .  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10 \%$ ,  $x_{\text{S}} = 30 \%$  at  $1000 \text{ C}$ .  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$ .

# Results – Sticky temperature



**Figure 15.** Liquid fraction in condensed phases. . Dashed lines refer to CFE, solid lines to EQ. T15 and T70 marked as horizontal lines.  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{Na}} = 10\%$ ,  $x_{\text{S}} = 30\%$  at 1000 C.  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} =$



**Figure 16.** Sticky temperature between T15 and T15 as function of volatility of sodium,  $x_{\text{Na}}$ , in the super-equilibrium of fume. CFE assumption.  $\lambda_{\text{furnace}} = 0.7$ . Volatility:  $x_{\text{S}} = 30\%$  at 1000 C.  $EF_{\text{K}} = 1.4$  and  $EF_{\text{Cl}} = 2.5$ .

# Discussion

- Difference of fume composition is obvious when comparing the results from thermodynamic equilibrium and CFE-super-equilibrium.
  - In line with previous studies, which has utilised dual approach for modelling the lower furnace to compensate the restriction of utilising thermodynamic equilibrium.
  - Super-equilibrium approach can be used for successfully limiting the volatility of sulphur at cold furnace as well as volatility of sodium at hot furnace.
  - In addition the higher volatility at temperature range (900 – 1100°C) can be described with proposed super-equilibrium method.
- Smaller differences is shown for char bed and smelt composition
  - Smaller difference in temperature range (900 -1100°C)
  - More obvious for very cold and very hot furnace
- Noticeable difference is in the condensing phases from the fume
  - The ratio of sulphur vs. carbonate is increasing with Super-EQ assumption
  - Sticky temperature decreases when amount of sodium in the fume is increasing
  - T15 declines 40-50°C and T70 ~ 10°C when amount of sodium is changed from 1% to 20%
- NOTE: Only fume is considered in this study as the amount carry-over particles in flue gas is assumed smaller when compared to fume.



# Conclusions #1

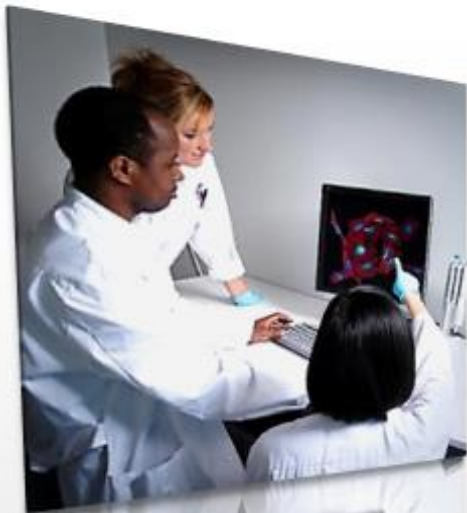
- CFE-Super-equilibrium method was successfully applied to thermodynamic model of black liquor combustion.
- Model consists of
  - Parameters for the amount of volatile Na and S
  - Enrichment factors for K and Cl
  - Virtual constraints to describe the super-equilibrium and connected to the compounds affinity to remain in fume.
  - Additional phase to describe the combusted black liquor as elements
- Model predicts
  - Fume and smelt properties based on the constrained equilibrium of lower furnace
  - Effects of higher volatility and enrichment of components to composition
  - Sticky temperatures of condensed phases from the fume.

## Conclusions #2

- Developed method does not describe the actual phenomena of volatilisation during the droplet in-flight or char bed burning, but relays the previous work and studies.
- By extending the chemical equilibrium system with constraints, it is possible to predict the measured excess of Na, K, S and Cl content in the fume.
  1. The exact principle of volatility can be implemented into the model
  2. Or measured amount of components can be forced to the fume
- Clear benefit of presented approach is that super-equilibrium, namely constrained local equilibrium, can be solved with single calculation step while obtaining chemical composition and enthalpic effects simultaneously.
- Ash chemistry of upper part of furnace can be solved with second calculation step to predict the condensed phases from the fume.
- A promising application for presented approach is to implement model as part of large scale process simulator.

# References

- [1] Enestam, S., Corrosivity of hot flue gases in the fluidized bed combustion of recovered waste wood, Dissertation, Åbo Akademi (2011).
- [2] Larson, E.D., Consonni, S., Katofsky, R.E., Campell, M., Iisa, K. and Frederick, W.J., A Cost-Benefit Assessment of Gasification-Based Biorefining in the Kraft Pulp and Paper Industry: Volume 3 Fuel Chain and National Cost-Benefit Analysis, (2006) 38.
- [3] Backman, R. and Hupa, M., Gasification of black liquor at elevated pressures - Thermodynamic analysis, (1990) 60.
- [4] Hupa, M., "Recovery boiler chemical principles", Proceedings, Tappi Kraft Recovery Short Course, St. Petersburg, FL, US (2008).
- [5] Hupa, M., Backman, R., Skrifvars, B. and Forssén, M., "Liquor-to-Liquor Differences in Combustion and Gasification Processes : Dust Composition and Melting Properties", Journal of Pulp and Paper Science, 27(12):416–422 (2001).
- [6] Salmenoja, K., Veli-Antti, K., Hupa, M. and Backman, R., "Chemical Balance of Non-Process Elements in Five Finnish Pulp Mills", Proceedings, International Chemical Recovery Conference, Charleston, SC, US (2004).
- [7] Mikkonen, P., Kauppinen, E.I., Pyykönen, J., Jokiniemi, J.K., Aurela, M., Vakkilainen, E.K., et al., "Alkali Salt Ash Formation in Four Finnish Industrial Recovery Boilers", Energy & Fuels, 13(4):778–795 (1999).
- [8] Janka, K., Wall, J. and Backman, R., "Prediction of dust content and properties in kraft recovery boilers: comparison of theory and experimental results", Pulp and Paper Canada, 105(1):46–50 (2004).
- [9] Vakkilainen, E.K., "Predicting Ash Properties in Recovery Boilers", Proceedings, International Chemical Recovery Conference, Williamsburg, VA, US (2010).
- [10] Lindberg, D., Thermochemistry and melting properties of alkali salt mixtures in black liquor conversion processes, Dissertation, Åbo Akademi (2007).
- [11] Backman, R., Eriksson, G. and Sundström, K., "The Recovery Boiler Advisor. Combination of practical experience and advanced thermodynamic modeling", Proceedings, 3rd Colloquium of Process Simulation, Espoo, Finland (1996).
- [12] Uloth, V., Richardson, B., Hogikyan, R. and Haynes, J., "Using a recovery boiler computer simulation to evaluate process alternatives for obtaining incremental recovery capacity", Tappi Journal, 75(11):137–147 (1992).
- [13] Järvinen, M.P., Kankkunen, A.P., Miikkulainen, P.H. and Heikkilä, V.P., "A One-Dimensional Flow Model of a Flashing Black Liquor Gun: Study of Vapor Generation Sub-Models", Proceedings, Swedish-Finnish Flame Days 2011, Piteå, Sweden, 1–14 (2011).
- [14] Mikkonen, P., Fly ash particle formation in kraft recovery boilers recovery boilers, Dissertation, Helsinki University of Technology (2000).
- [15] Engblom, M., Modeling and Field Observations of Char Bed Processes in Black Liquor Recovery Boilers, Dissertation, Åbo Akademi (2010).
- [16] Grace, T., Walsh, A., Jones, A., Sumnicht, D. and Farrington, T., "Three-dimensional mathematical model of the kraft recovery furnace", Proceedings, International Chemical Recovery Conference, Ottawa, ON, CA (1989).
- [17] Leppänen, A., Välimäki, E. and Oksanen, A., "Modeling fine particles and alkali metal compound behavior in a kraft recovery boiler", Tappi Journal, 11(7):9–14 (2012).
- [18] VTT, Knowpulp, (2011).
- [19] Smith, W.R. and Missen, R.W., Chemical reaction equilibrium analysis: theory and algorithms, Krieger Publishing Company, Malabar, FL, US (1991).
- [20] Koukkari, P., Penttilä, K., Hack, K. and Petersen, S., "CHEMSHEET – An Efficient Worksheet Tool for Thermodynamic Process Simulation", In: Microstructures, Mechanical Properties and Processes, Y. Bréchet (Ed.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2005).
- [21] Bale, C.W., Bélisle, E., Chartrand, P., Decterov, S. a., Eriksson, G., Hack, K., et al., "FactSage thermochemical software and databases — recent developments", Calphad, 33(2):295–311 (2009).
- [22] Koukkari, P. and Pajarre, R., "Introducing mechanistic kinetics to the Lagrangian Gibbs energy calculation", Computers & Chemical Engineering, 30(6-7):1189–1196 (2006).
- [23] Koukkari, P. and Pajarre, R., "A Gibbs energy minimization method for constrained and partial equilibria", Pure and Applied Chemistry, 83(6):1243–1254 (2011).
- [24] Kangas P, Pajarre R, Nappa M, Koukkari P. Multi-phase thermodynamic modelling of pulp suspensions: Review of the methodology. Nord Pulp Pap Res J 2012;27:604–12.
- [25] Kangas P, Koukkari P, Lindberg D, Hupa M. Modelling black liquor combustion with the constrained Gibbs energy method. 8th International Black Liquor Colloquium, Belo Horizonte, Brazil: 2013.
- [26] Kangas P, Koukkari P, Hannula I. Modelling Super-Equilibrium in Biomass Gasification With the Constrained Gibbs Energy Method. AIChE 2013 Annual meeting, San Francisco, CA, US: 2013.
- [27] Alberty, R.A., "Thermodynamics of the formation of benzene series polycyclic aromatic hydrocarbons in a benzene flame", The Journal of Physical Chemistry, 93(8):3299–3304 (1989).
- [28] Keck, J.C., "Rate-controlled constrained-equilibrium theory of chemical reactions in complex systems", Progress in Energy and Combustion Science, 16(2):125–154 (1990).
- [29] Koukkari, P., "A physico-chemical method to calculate time-dependent reaction mixtures", Computers & Chemical Engineering, 17(12):1157–1165 (1993).



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