PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI UNIVERSITY

Thermodynamic modeling of biomass combustion and ash chemistry applications

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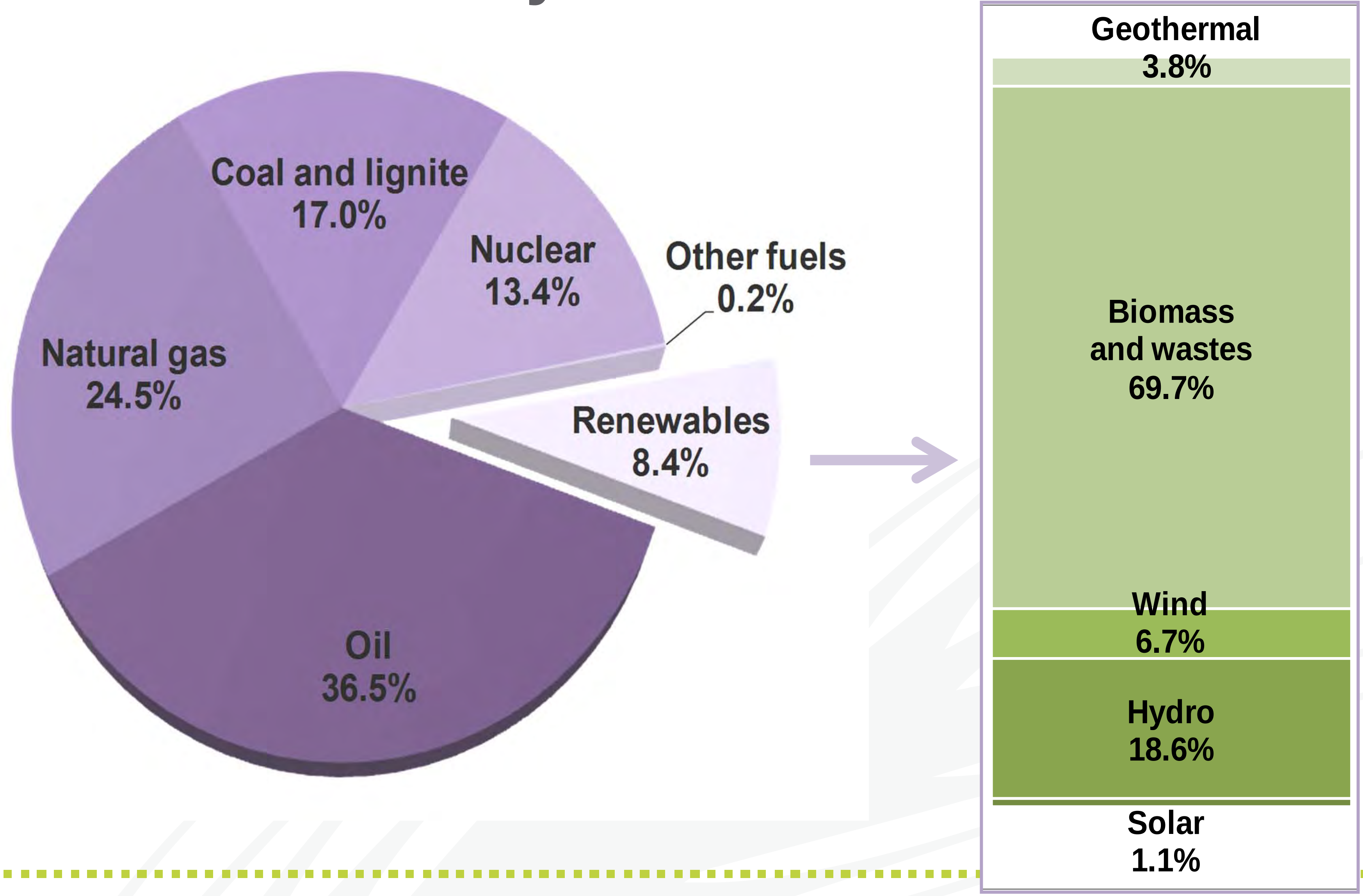
EU-27, gross inland energy consumption
Primary raw materials



Source: European Commission's Market Observatory data for 2008

Biofuels – Waste derived fuels – "Opportunity fuels"

- Woodchips
- Saw dust
- Bark

- Forest residues
- Annual crops
- Prunings
- Shells, husks & hulls
- Olive stones

- Biorefinery residues
- Pulp & paper process by-products

- Refuse derived fuels (RDF)
- Waste sludges
- Recovered waste wood
- Meat and bone meal
- Chicken litter

Ash Forming Matter in Biomass Combustion – Research Topics

- Characterization of AFM
- Release of AFM in furnace
- Fly Ash Formation
- Bed/Grate Reactions
- Fouling
- Superheater Corrosion
- Understanding Fuel Mixtures

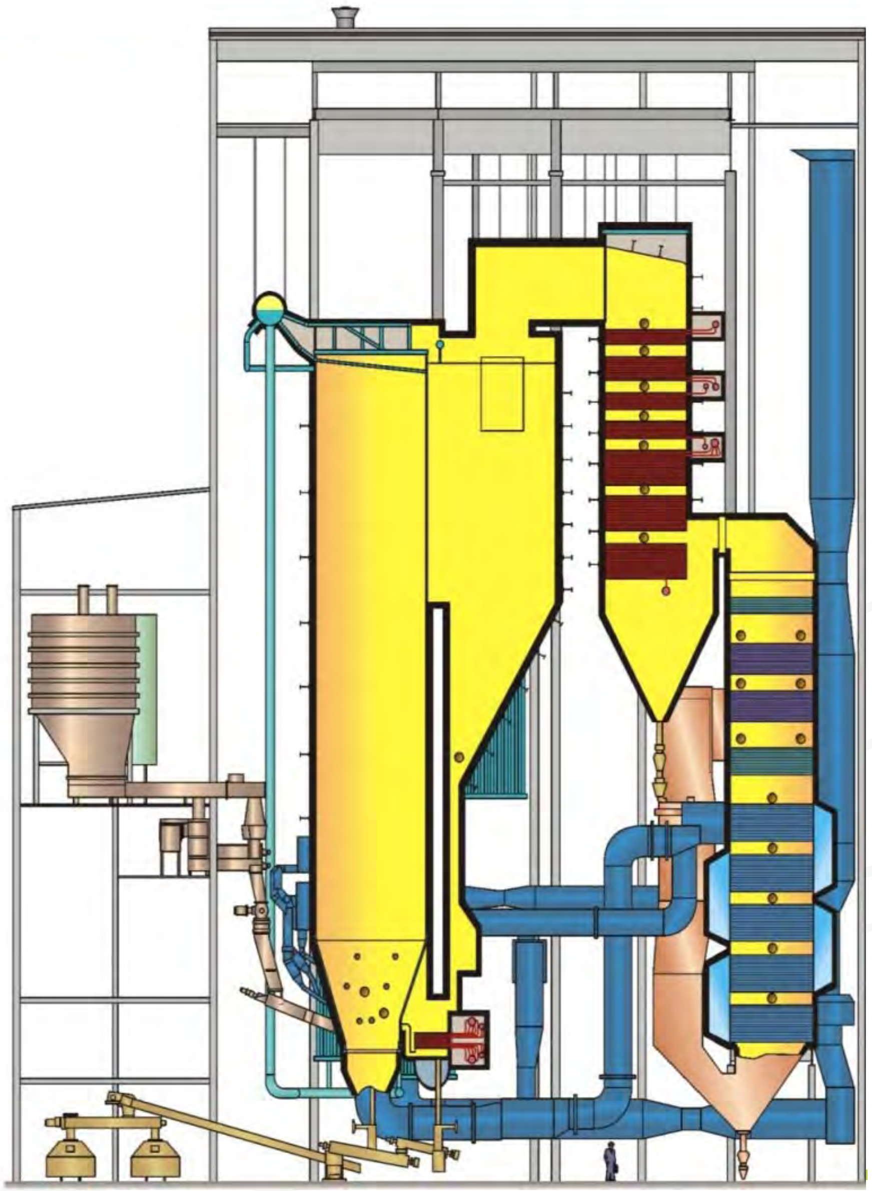
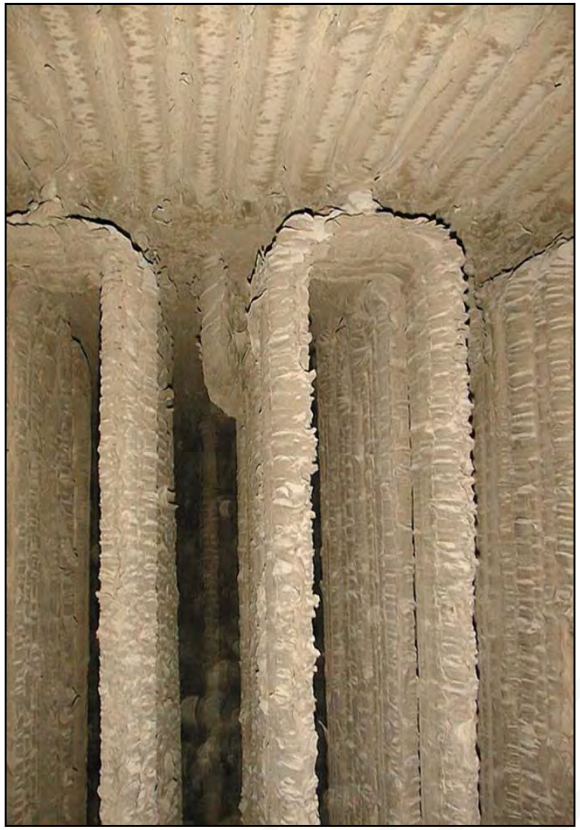


Figure courtesy: Mälarenergi Ab & Foster Wheeler

Fouling and corrosion due to unsuitable fuel mix



Thermodynamic modeling & Ash chemistry

Ash deposition

Bed agglomeration

Superheater corrosion

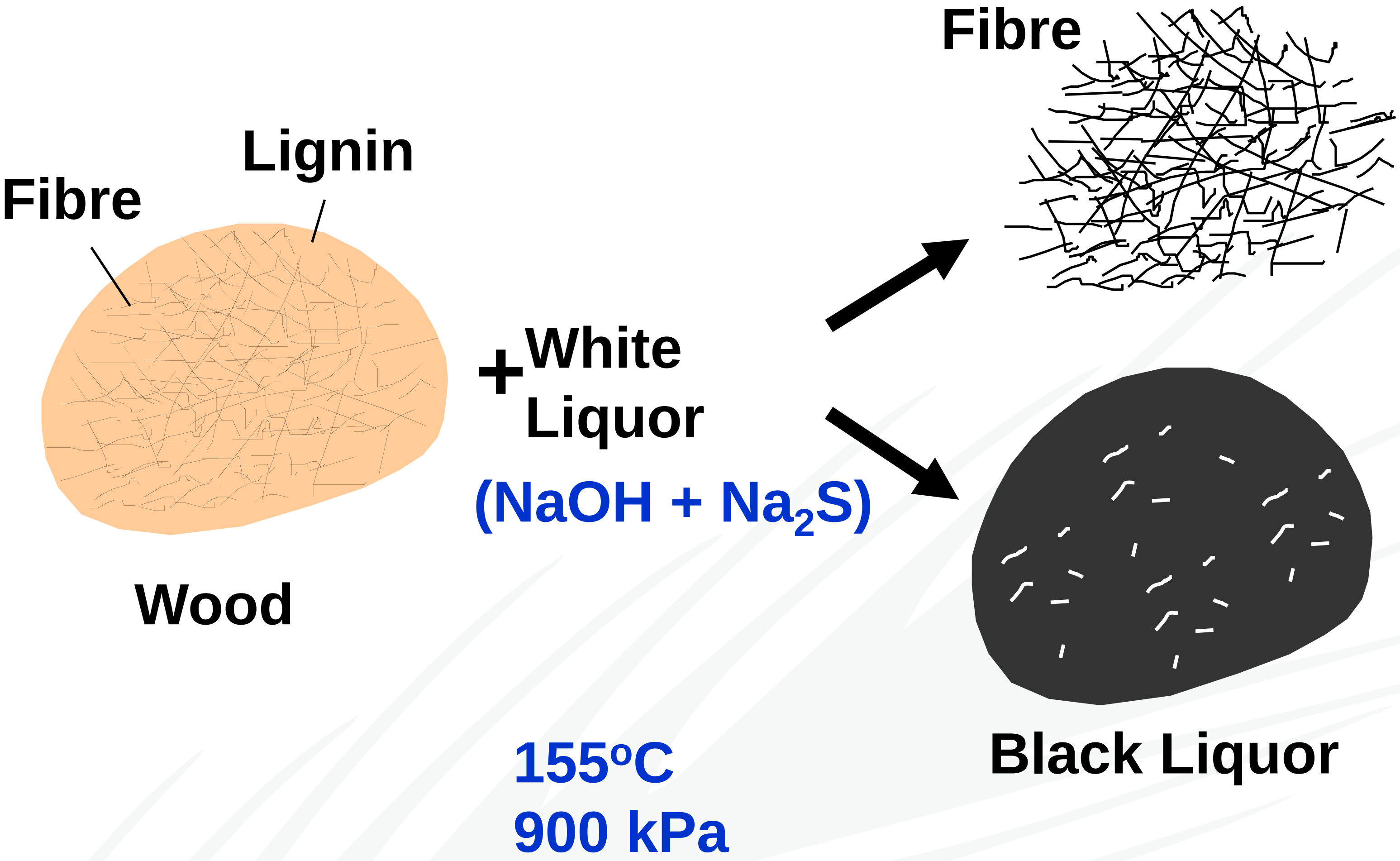
Furnace slagging

Trace element emissions

Black liquor combustion

Example
Black liquor recovery boiler

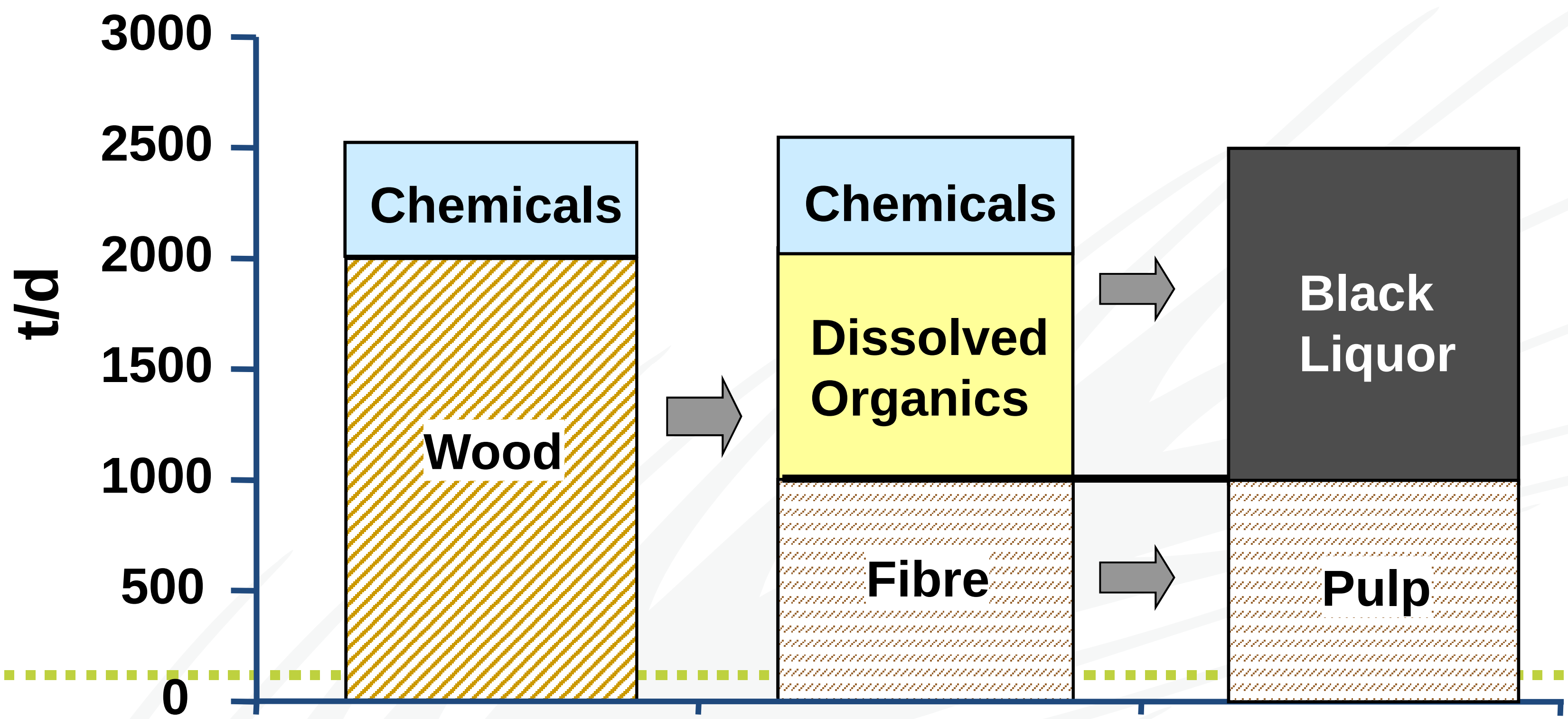
Kraft Pulping Process



A 1000 t/d Kraft Pulp Mill

produces 1500 t/d BL d.s.

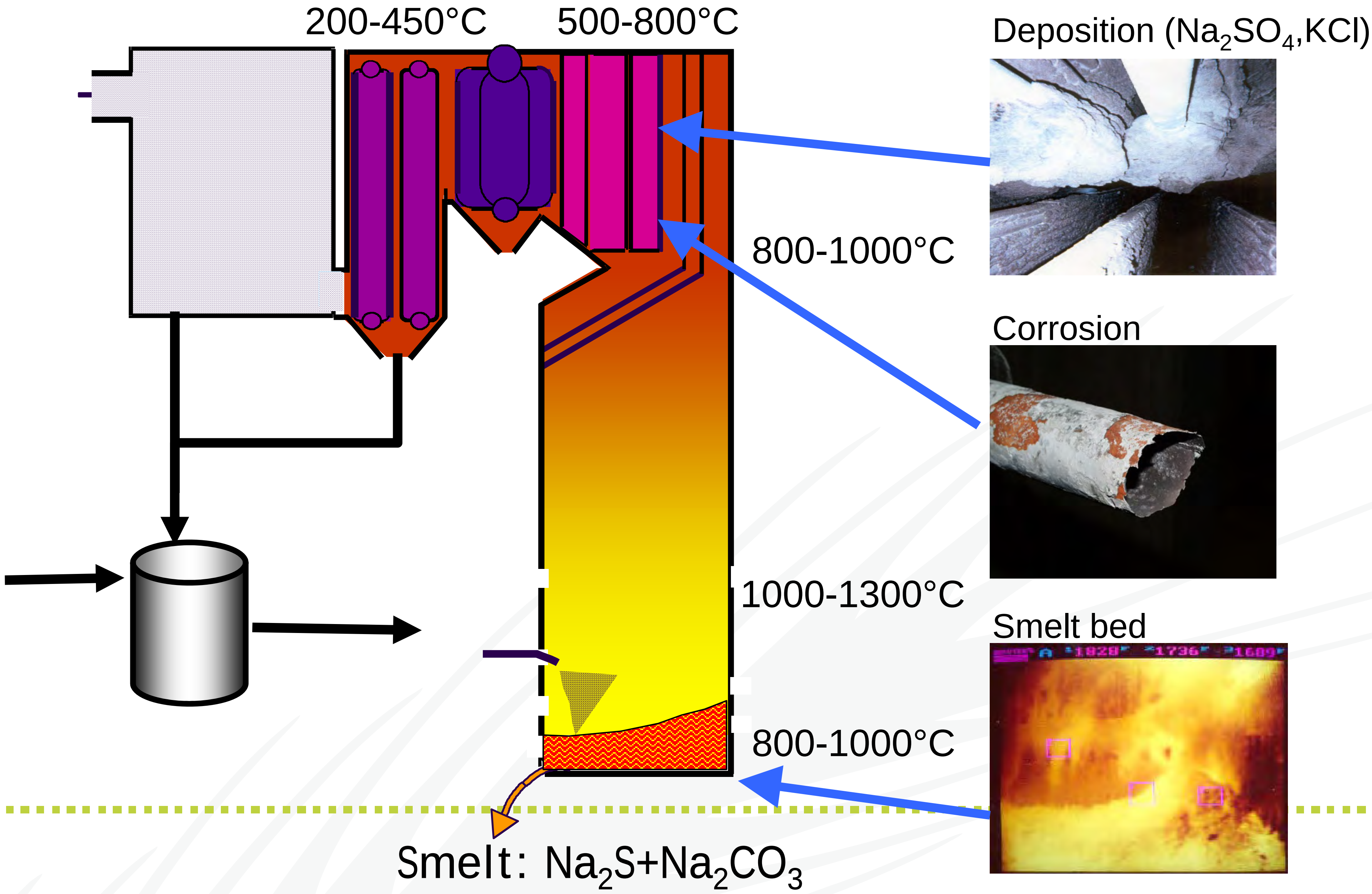
8000 ~ 10,000 t/d weak black liquor

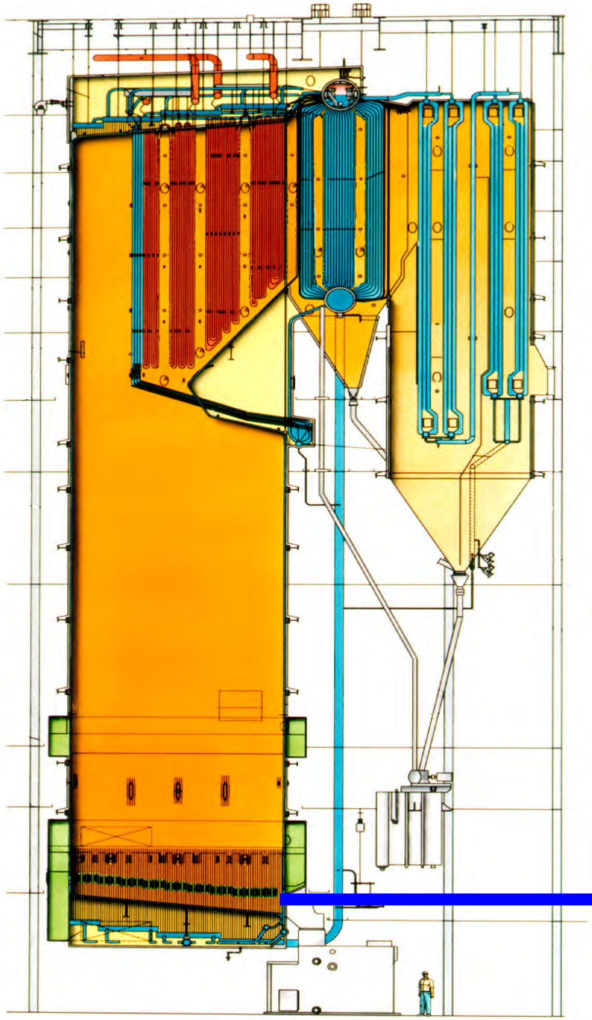


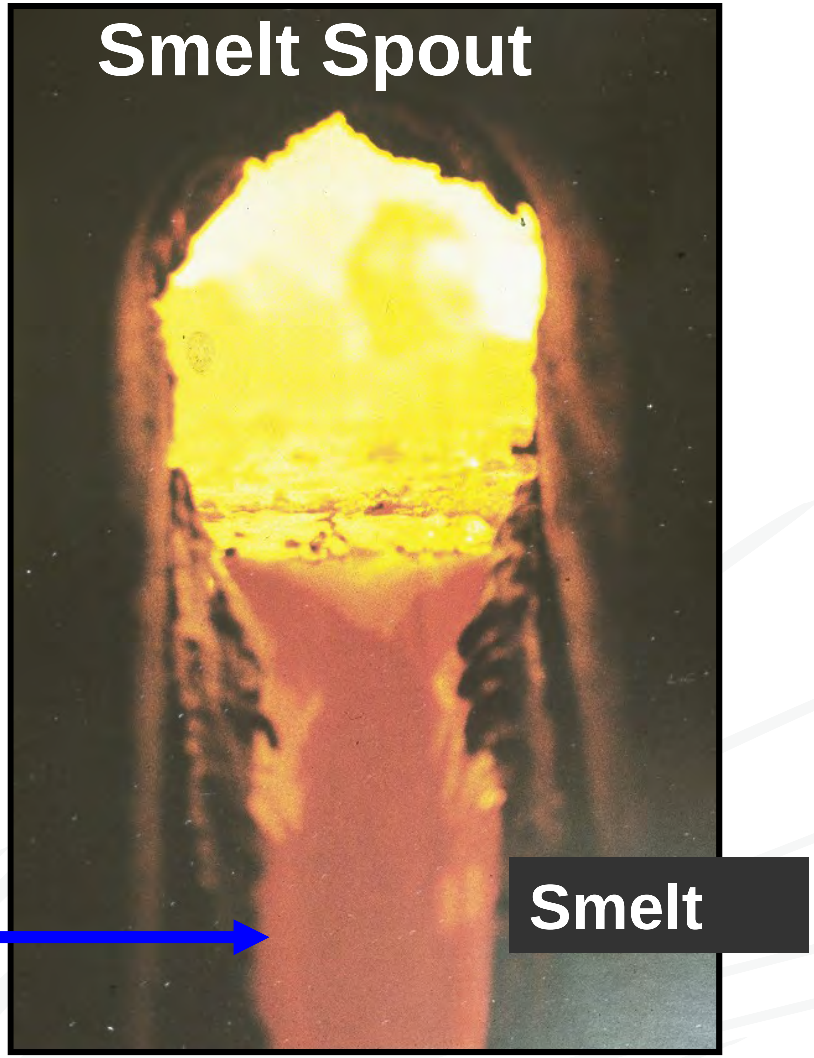
As-Fired Black Liquor Composition (750 liquor samples; All Wood Species)

		Typical	Range
	Solids content, %	**72**	**65 – 85**
	HHV, MJ/kg	**13.9**	**12.5 – 15.5**
Composition	**C, wt% d.s.**	**33.9**	**30 – 40**
	H	**3.4**	**3.2 – 4.0**
	O	**35.8**	**34 – 38**
	Na	**19.6**	**17 – 22**
	S	**4.6**	**3.6 – 5.6**
	K	**2.0**	**1 – 3**
	Cl	**0.5**	**0.1 – 4**

Molten salts in the recovery boiler





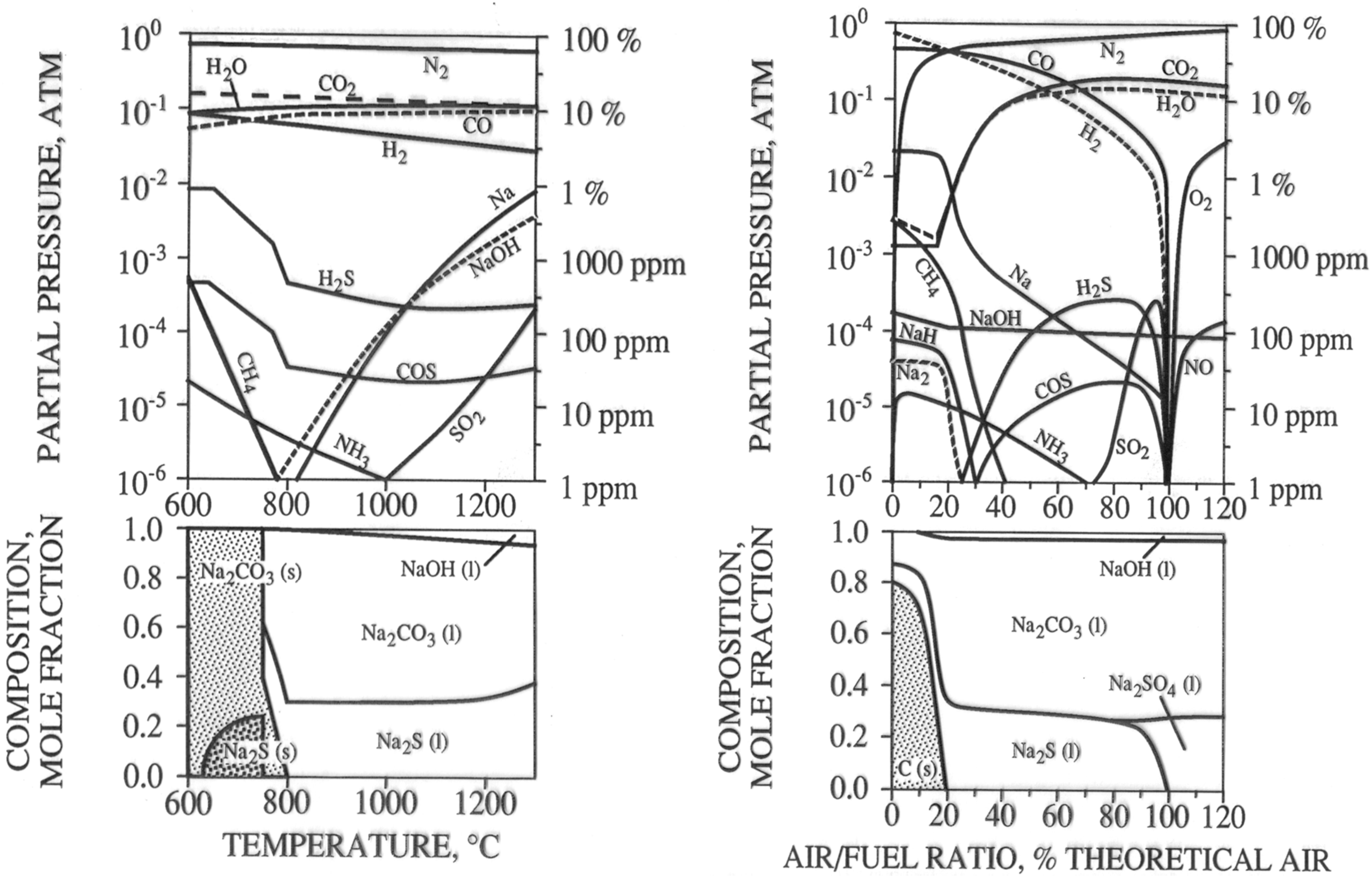


Na_2CO_3 + Na_2S

Equilibria with Molten Phases: Black Liquor Recovery Boiler and Alkali Salts

Lars Pejryd & Mikko Hupa (1984) Bed and furnace gas composition in recovery boilers – advanced equilibrium calculations. *Tappi Pulping Conference*

- Equilibrium modeling of furnace gas and smelt bed of a kraft recovery boiler
- Non-ideal interactions for liquid Na_2CO_3-Na_2S optimized by Gunnar



PARTIAL PRESSURE, ATM
COMPOSITION, MOLE FRACTION
TEMPERATURE, °C
N2
H2O
CO2
CO
H2
Na
NaOH
H2S
COS
CH4
NH3
SO2
Na2CO3 (s)
NaOH (l)
Na2CO3 (l)
Na2S (s)
Na2S (l)
VOLUME CONCENTRATION
AIR/FUEL RATIO, % THEORETICAL AIR
O2
NaH
Na2
NO
Na2SO4 (l)
C (s)
100 %
10 %
1 %
1000 ppm
100 ppm
10 ppm
1 ppm

Thermodynamic databases for alkali salts

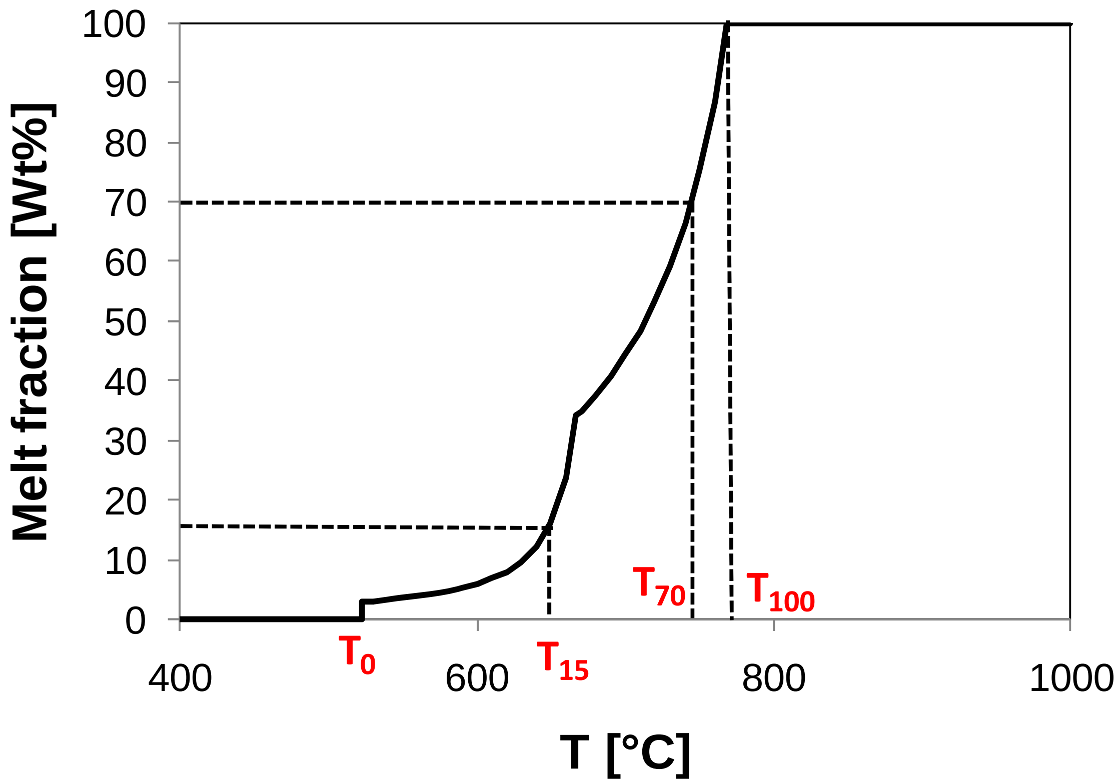
Thermodynamic properties of alkali salts

- Na-K-S-C-O-Cl-H system re-evaluated
  - Lindberg (2007) *Thermochemistry and melting properties of alkali salt mixtures (PhD thesis*)
  - Lindberg, Backman & Chartrand. (2007) Journal of Chemical Thermodynamics. *Thermodynamic evaluation and optimization of the (NaCl + Na_2SO_4 + Na_2CO_3 + KCl + K_2SO_4 + K_2CO_3)*
- Covers all Na-K components from reducing to oxidizing conditions
- FTPulp database in Factsage

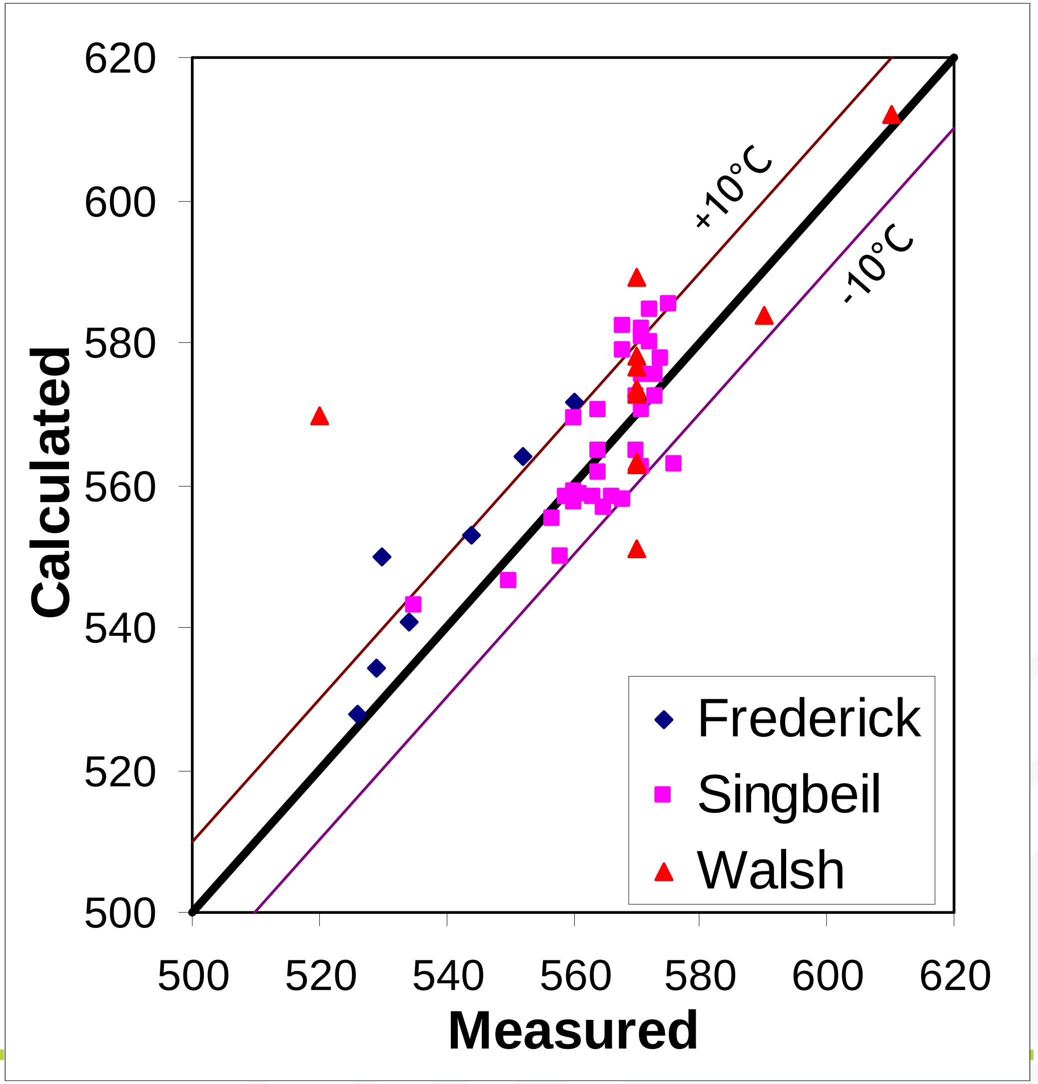
My PhD defense in 2007

Melting properties of alkali salts & characteristic temperatures

- T_0, First melting temperature: Corrosion
- T_{15}, Sticky temperature: Deposition
- T_{70}, Flow temperature: Deposit buildup
- T_{100}, Complete melting temperature: Flow properties



Solidus temperature (T_0) of superheater deposits from BL recovery boilers

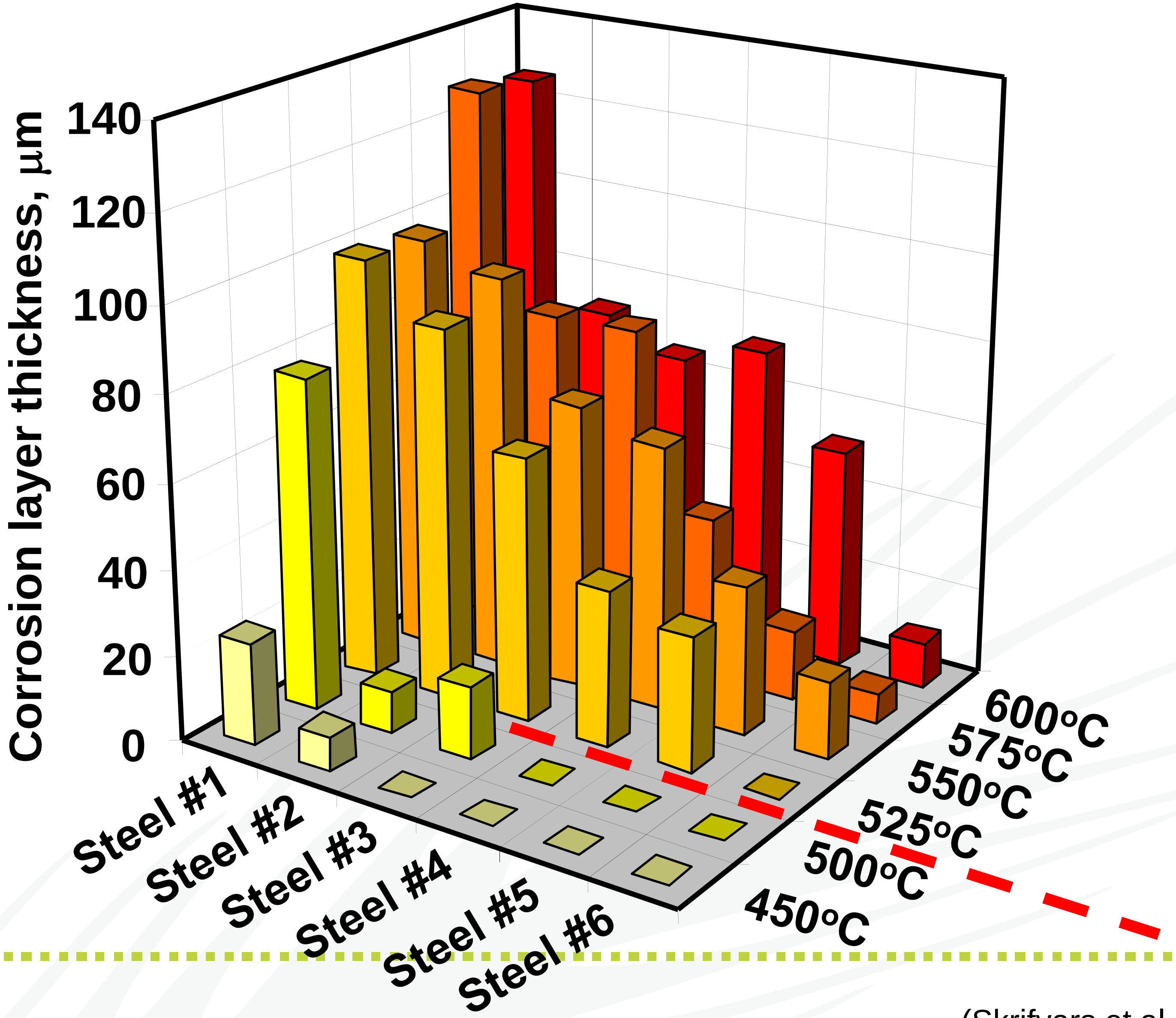


Solidus measured with DTA

Deposits contain Na^+,K^+/SO_4^{2-},CO_3^{2-},Cl^-

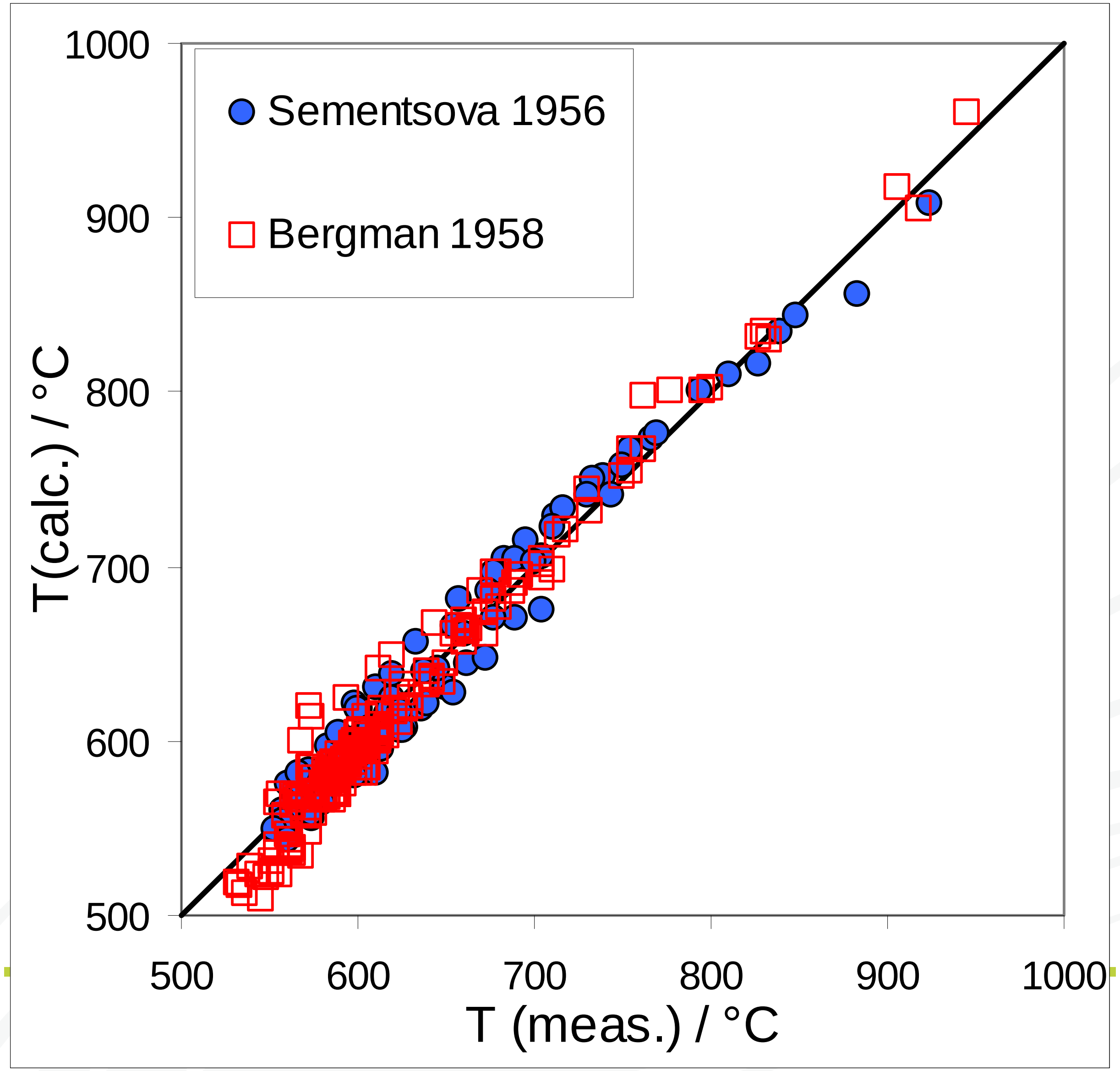
Thermodynamic model predicts solidus (T_0) within ±10°C

$(Na,K)_2SO_4$ + 1.3% Cl, T_0=522°C



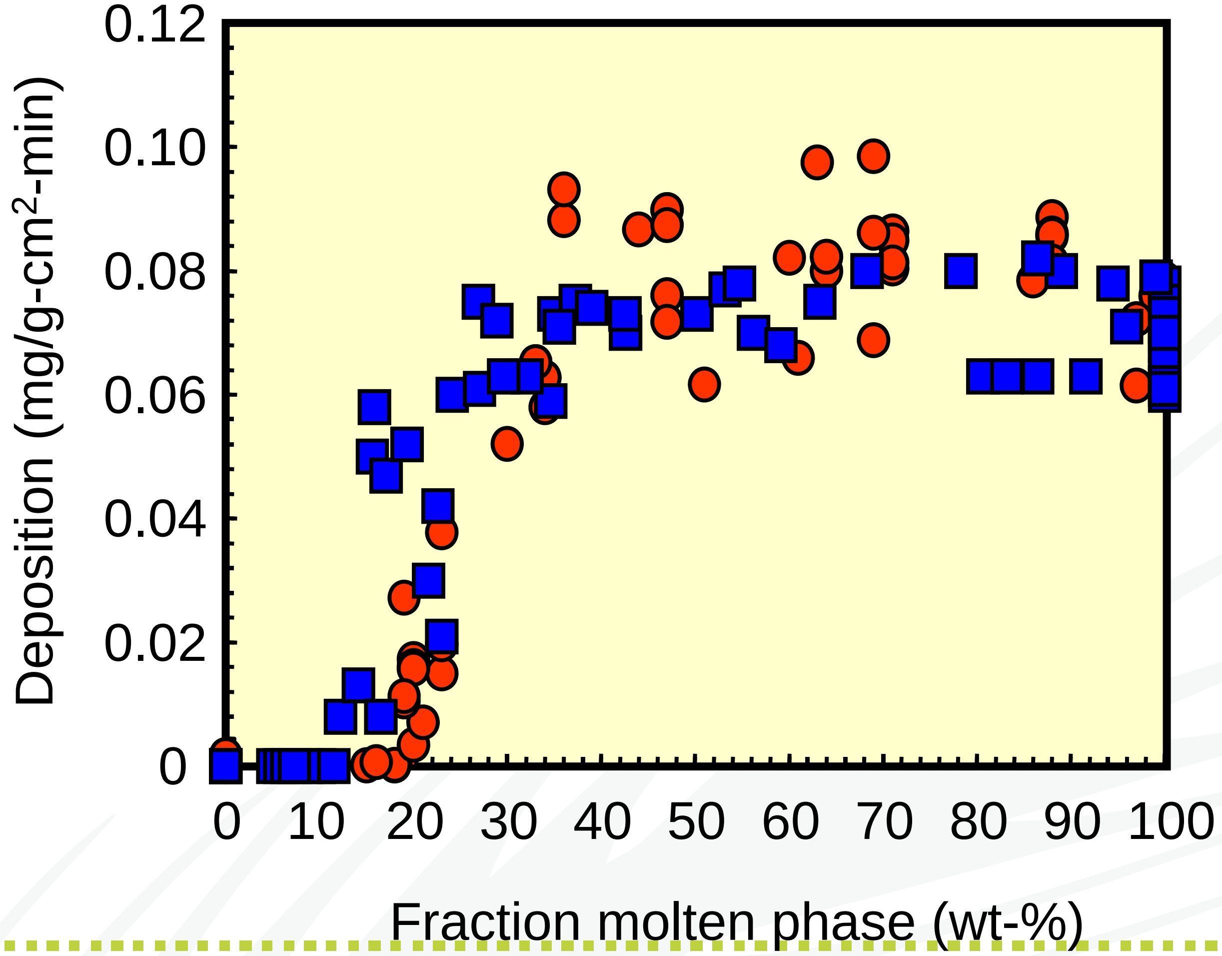
(Skrifvars et al. 2008)

Liquidus temperatures (T_{100}) of Na^+,K^+/Cl^-,SO_4^{2-},CO_3^{2-} mixtures



Stickiness of Partially Molten Particles

Entrained Flow Reactor Tests in Toronto



(Tran et al. 2002)

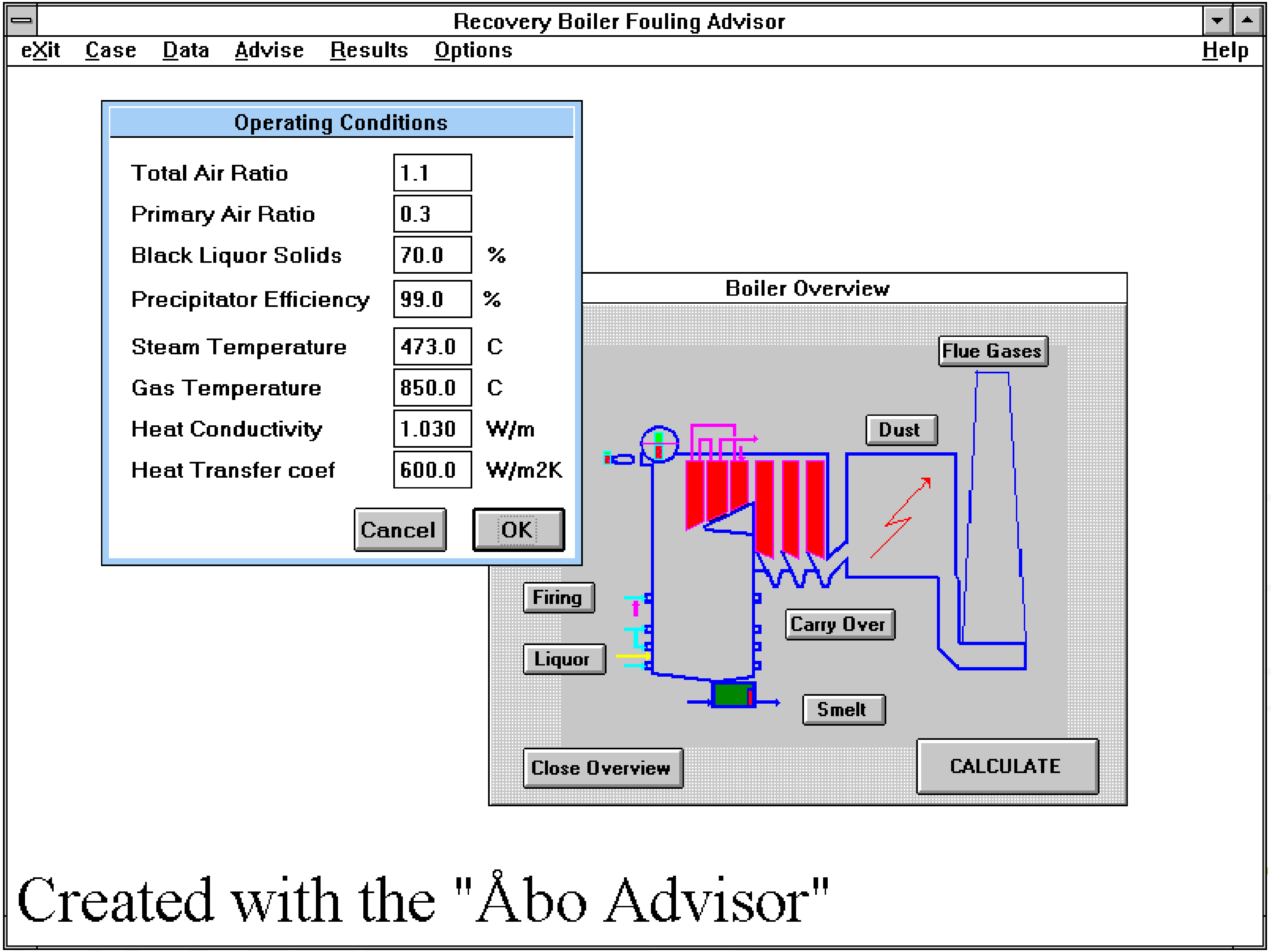
Åbo Black Liquor Recovery Boiler Advisor

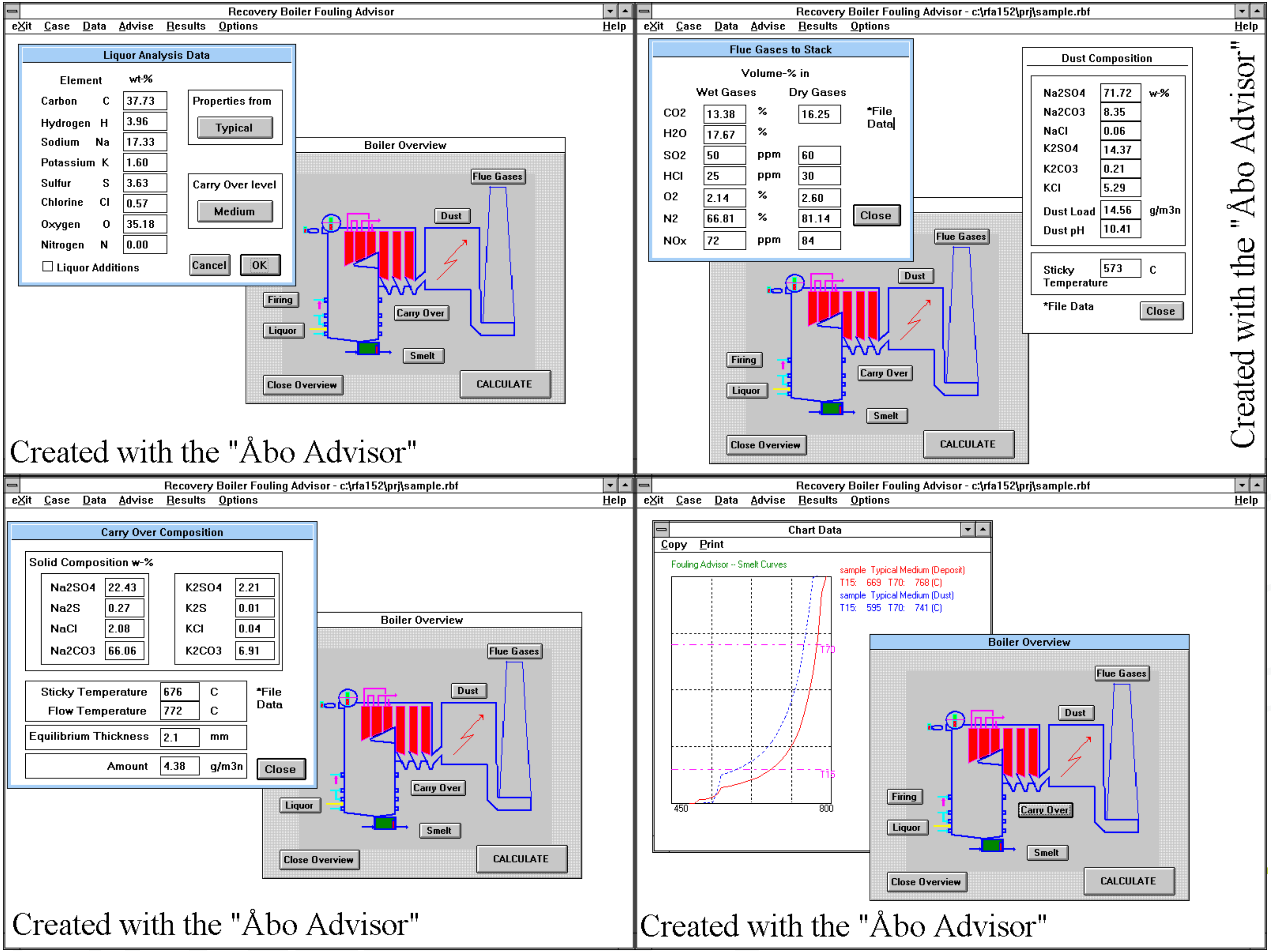
- ***Rainer Backman, Gunnar Eriksson, Kaj Sundström:*** The Recovery Boiler Advisor - Combination of Practical Experience and Advanced Thermodynamic Modelling, Proceedings: *3rd Colloquium on Process Simulation*, June 12-14, 1996

- An application of ChemApp on the chemical processes in the kraft recovery boiler

- Windows-based program for boiler designers and operators to predict chemical processes in the furnace and in flue gas channels

- One-dimensional, multi-stage chemistry model using chemical equilibrium calculations, physical models for deposit behavior and experimental information for combustion characteristics


Recovery Boiler Fouling Advisor
eXit
Case
Data
Advise
Results
Options
Help
Operating Conditions
Total Air Ratio 1.1
Primary Air Ratio 0.3
Black Liquor Solids 70.0 %
Precipitator Efficiency 99.0 %
Steam Temperature 473.0 C
Gas Temperature 850.0 C
Heat Conductivity 1.030 W/m
Heat Transfer coef 600.0 W/m2K
Cancel
OK
Boiler Overview
Flue Gases
Dust
Firing
Carry Over
Liquor
Smelt
Close Overview
CALCULATE
Created with the "Åbo Advisor"

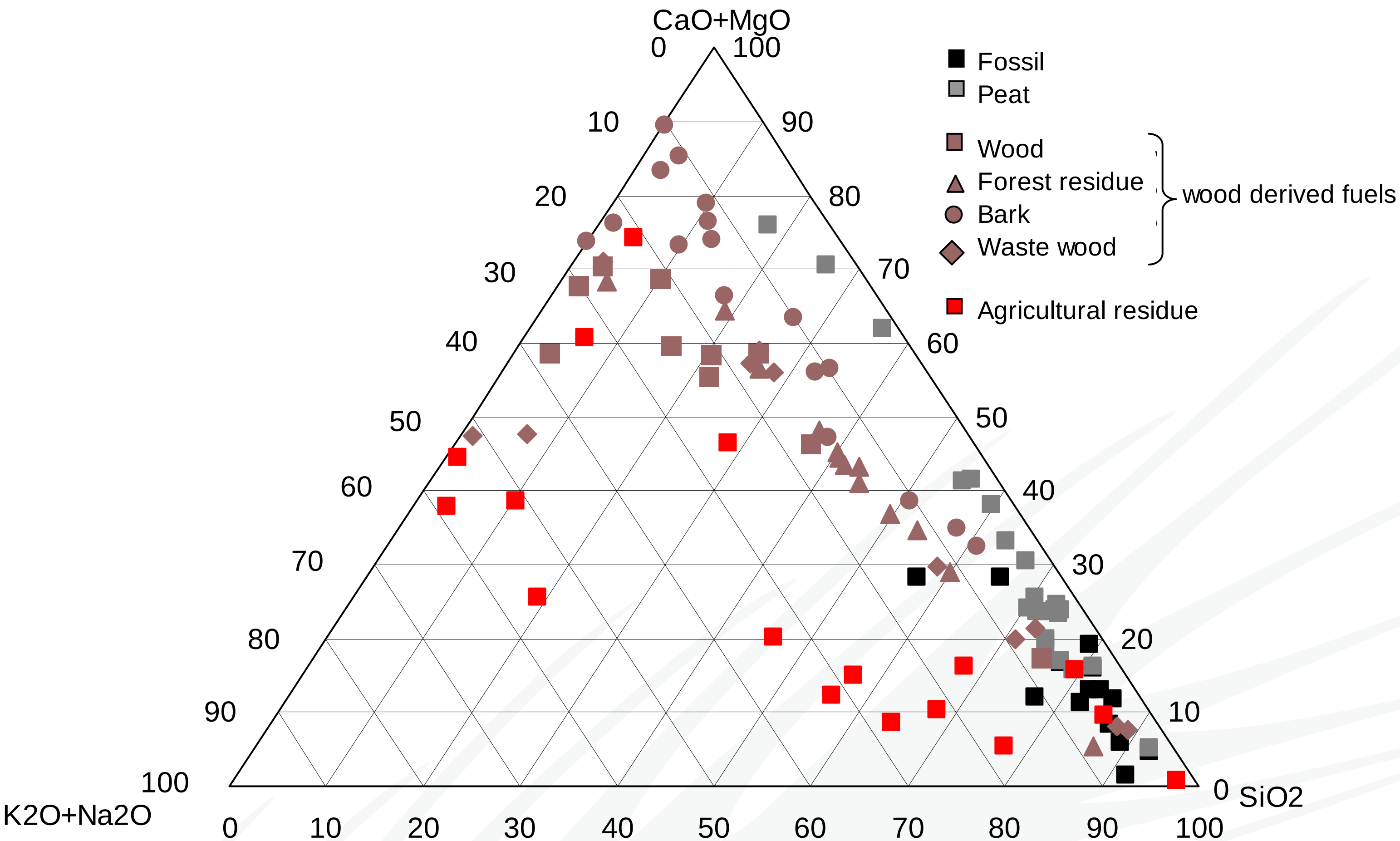

Recovery Boiler Fouling Advisor
eXit Case Data Advise Results Options Help
Liquor Analysis Data
Element wt-%
Carbon C 37.73
Hydrogen H 3.96
Sodium Na 17.33
Potassium K 1.60
Sulfur S 3.63
Chlorine Cl 0.57
Oxygen O 35.18
Nitrogen N 0.00
Liquor Additions
Properties from
Typical
Carry Over level
Medium
Cancel
OK
Boiler Overview
Flue Gases
Dust
Firing
Liquor
Carry Over
Smelt
Close Overview
CALCULATE
Created with the "Åbo Advisor"
Recovery Boiler Fouling Advisor - c:\rfa152\prj\sample.rbf
Flue Gases to Stack
Volume-% in
Wet Gases
Dry Gases
CO2 13.38 % 16.25
H2O 17.67 %
SO2 50 ppm 60
HCl 25 ppm 30
O2 2.14 % 2.60
N2 66.81 % 81.14
NOx 72 ppm 84
*File Data
Close
Dust Composition
Na2SO4 71.72 w-%
Na2CO3 8.35
NaCl 0.06
K2SO4 14.37
K2CO3 0.21
KCl 5.29
Dust Load 14.56 g/m3n
Dust pH 10.41
Sticky Temperature 573 C
*File Data
Close
Created with the "Åbo Advisor"
Carry Over Composition
Solid Composition w-%
Na2SO4 22.43
Na2S 0.27
NaCl 2.08
Na2CO3 66.06
K2SO4 2.21
K2S 0.01
KCl 0.04
K2CO3 6.91
Sticky Temperature 676 C
Flow Temperature 772 C
*File Data
Equilibrium Thickness 2.1 mm
Amount 4.38 g/m3n
Close
Created with the "Åbo Advisor"
Chart Data
Copy Print
Fouling Advisor -- Smelt Curves
sample Typical Medium (Deposit)
T15: 669 T70: 768 (C)
sample Typical Medium (Dust)
T15: 595 T70: 741 (C)
T70
T15
450
800
Created with the "Åbo Advisor"

Why thermodynamic modeling is useful for BL combustion

- Well-defined ”ash” chemistry (Na-K salts)
- Alkali salts have good contact in smelt bed
- High liquid content in inorganic particles down to 500 °C + molten phase has low viscosity → fast reactions
- Concepts T_{15} and T_{70} work for recovery boilers

Example
Biomass and waste boilers

Major ash-forming elements in different fuels



ÅA fuel database

Ash phases

Silicates

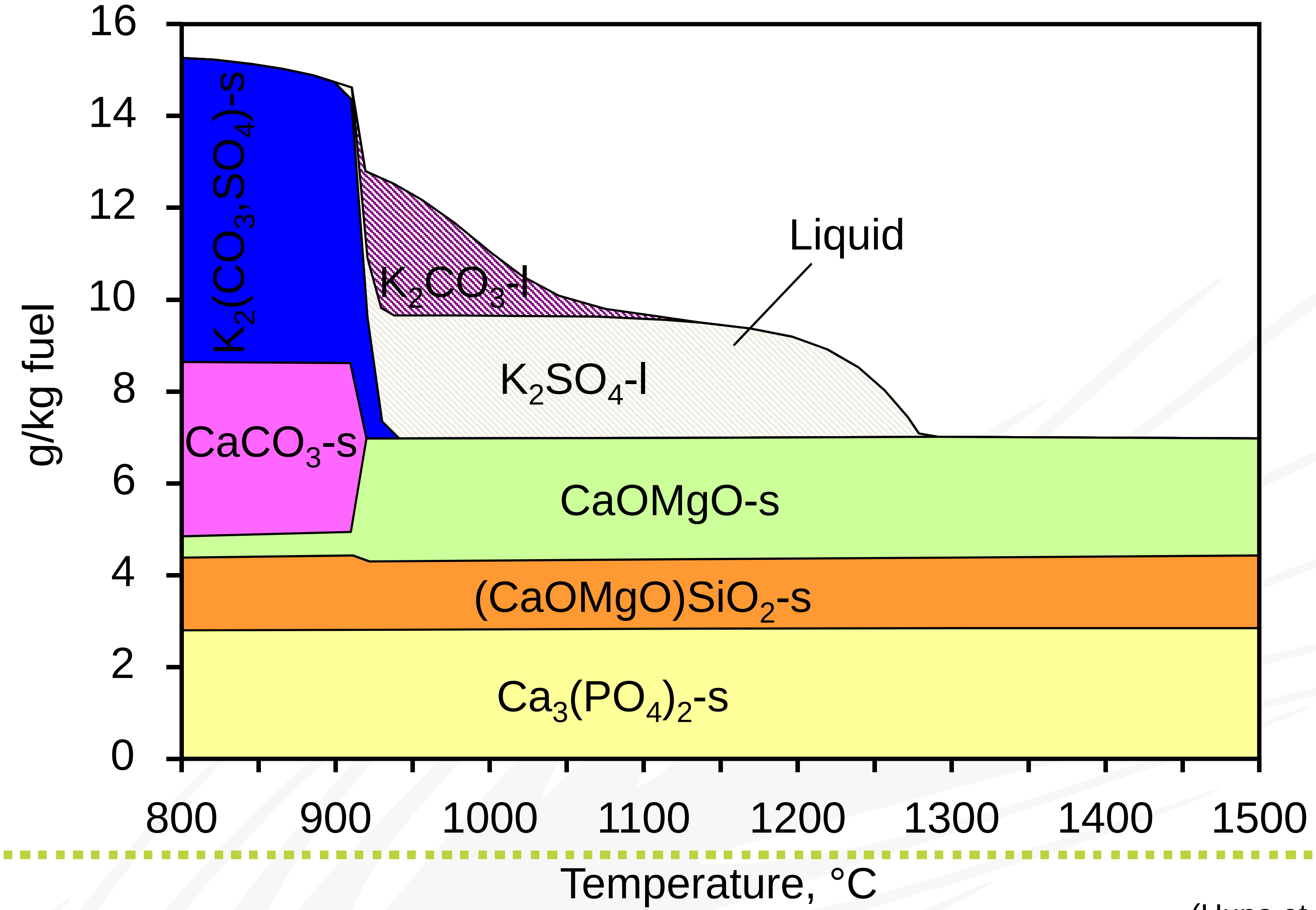
- Minerals in fuels
- Polymeric phases
- Ex. $KAlSi_3O_8$
- High viscosity liquid
- Quasichemical or associate models for thermodynamics

Salt-like phases

- Various formation reactions
- Simple ionic phases
- Examples KCl, $CaSO_4$
- Low viscosity liquid
- Sublattice models for thermodynamics

Fly Ash Composition of *Salix*

Multicomponent Multiphase Thermodynamic Calculation



(Hupa et al. 1999)

Availability of thermodynamic data

Accurate existing data

- Low-alkali silicates (coal, peat)
- Alkali salt mixtures (black liquor)
- Selected Na-K-Ca-Mg-Zn-Pb salt mixtures (on-going) (biomass, waste)

Improvements needed

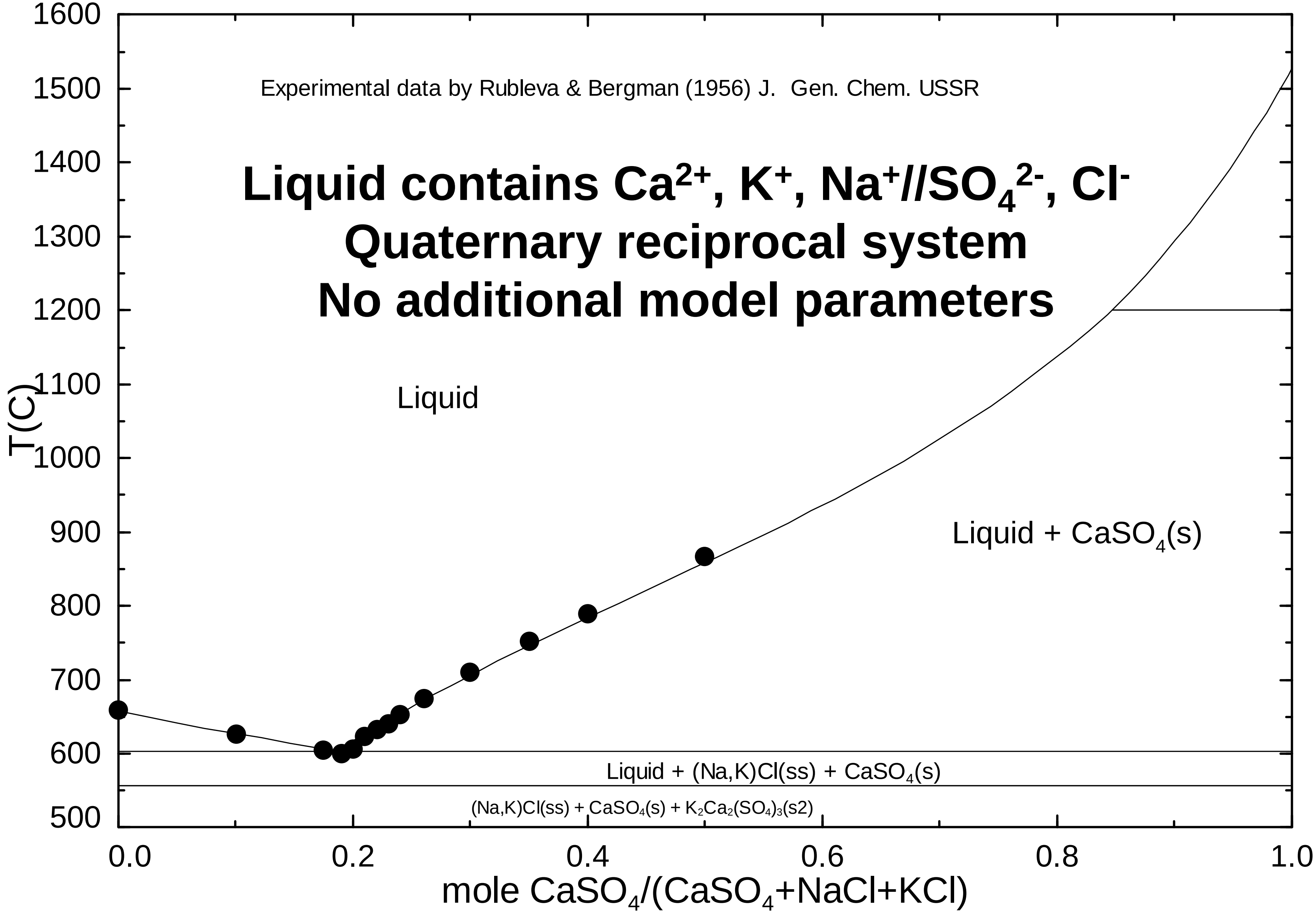
- K_2O-rich silicates (straw)
- Phosphate mixtures (on-going) (agricultural fuels)
- Unified database for heavy metals

Molten salts

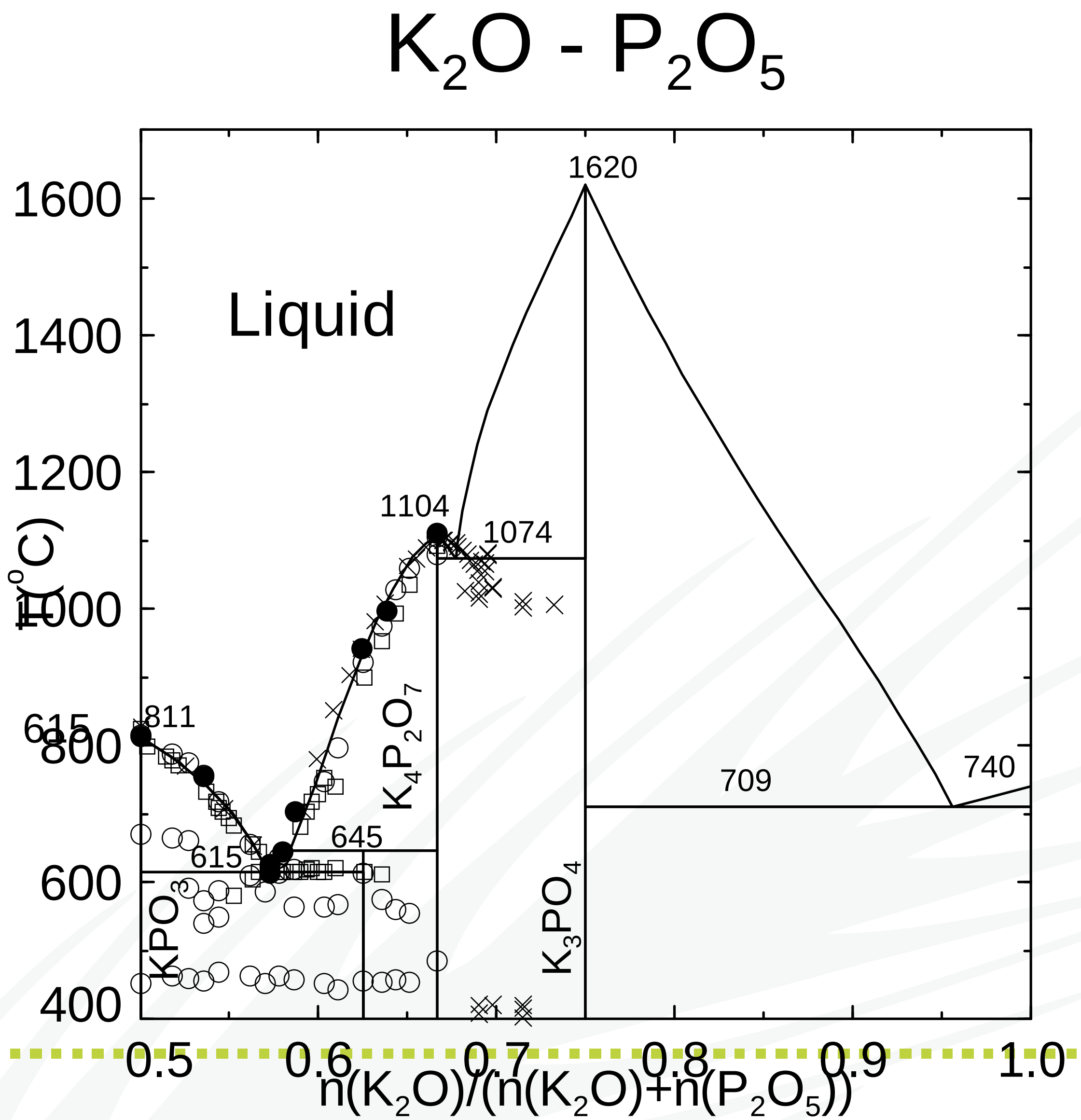
On-going and future developments

- Addition of **Ca-Mg-Pb-Zn-P** to **Na-K-S-C-O-Cl-H** system underway to cover all major salt-like phases in biomass and waste combustion
- New approach to include phosphorus in the liquid phase

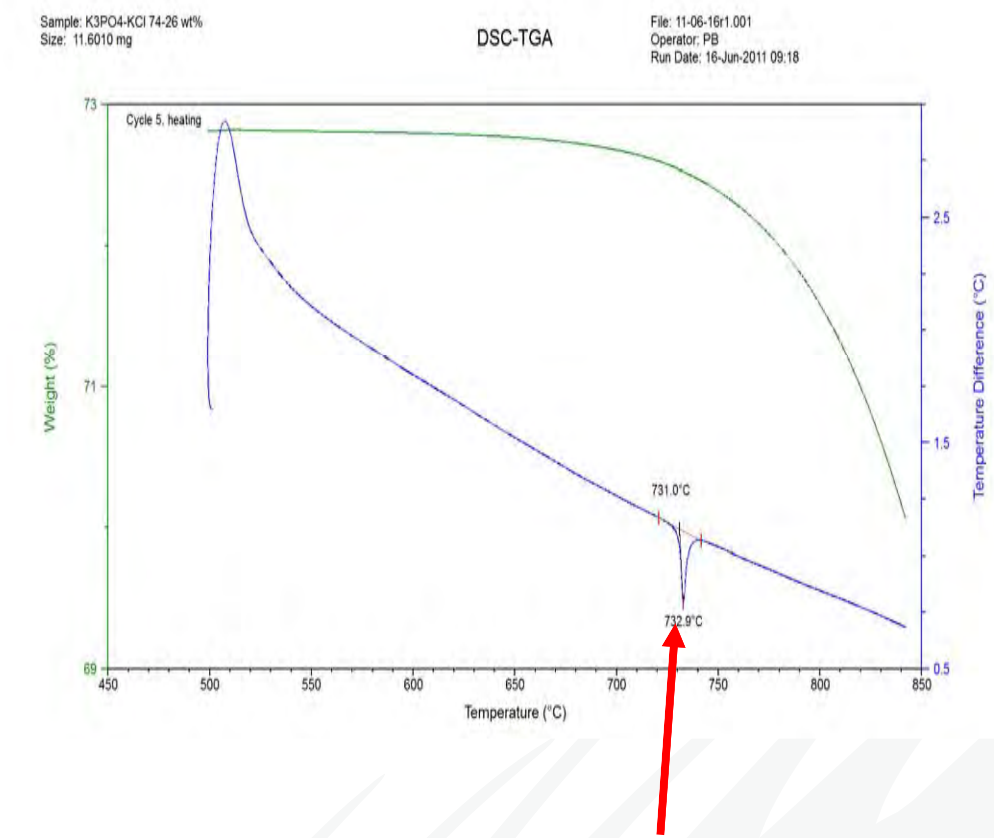
$CaSO_4$ - (NaCl+KCl)

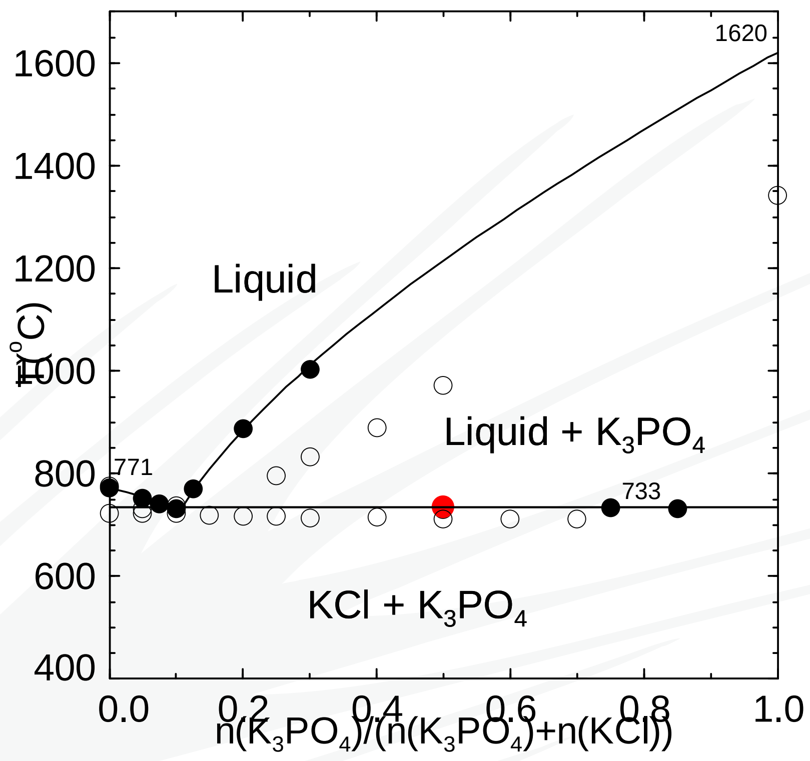


Phosphate chemistry – new results



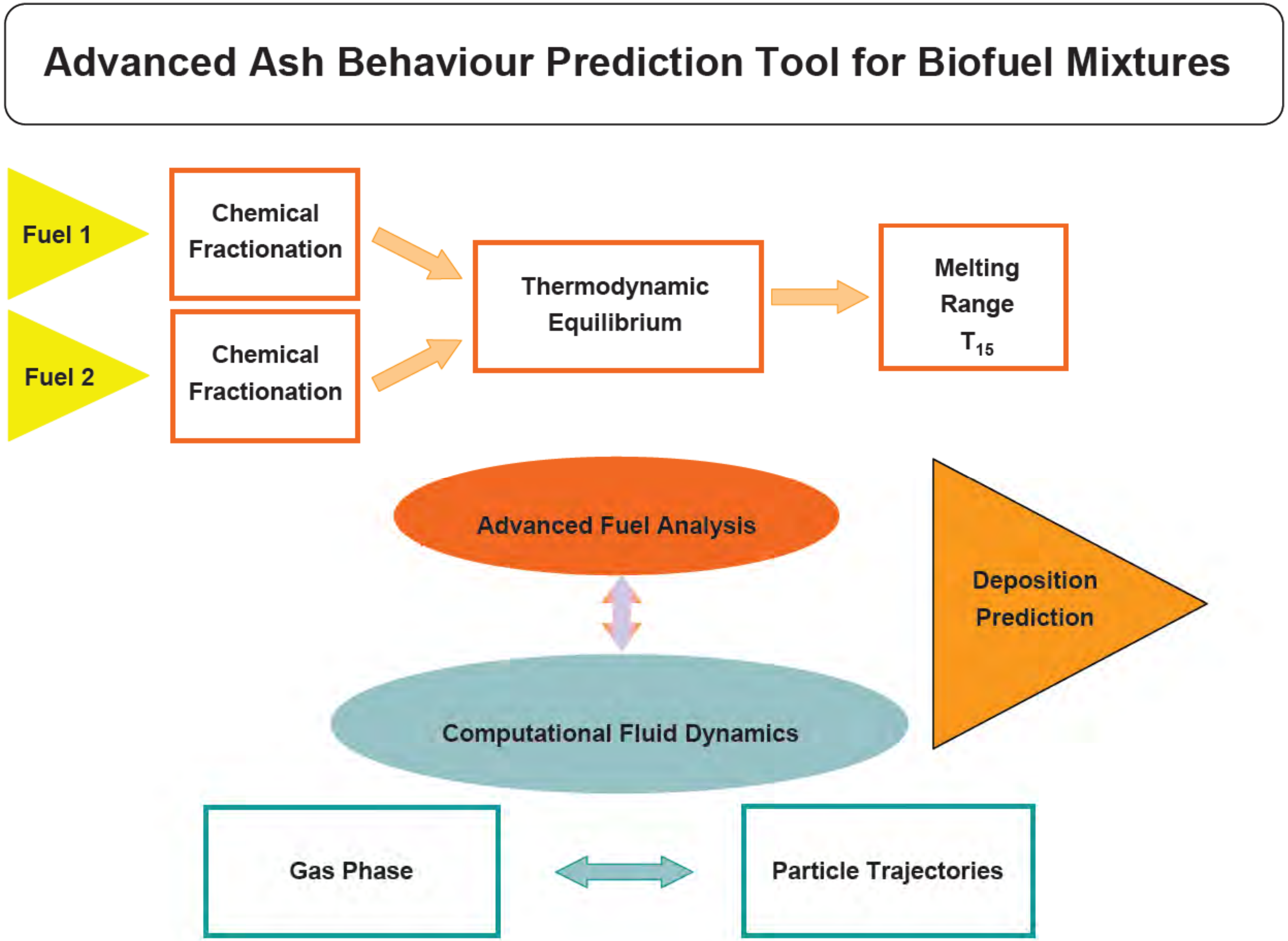
K_3PO_4-KCl mixture
Model vs experiment





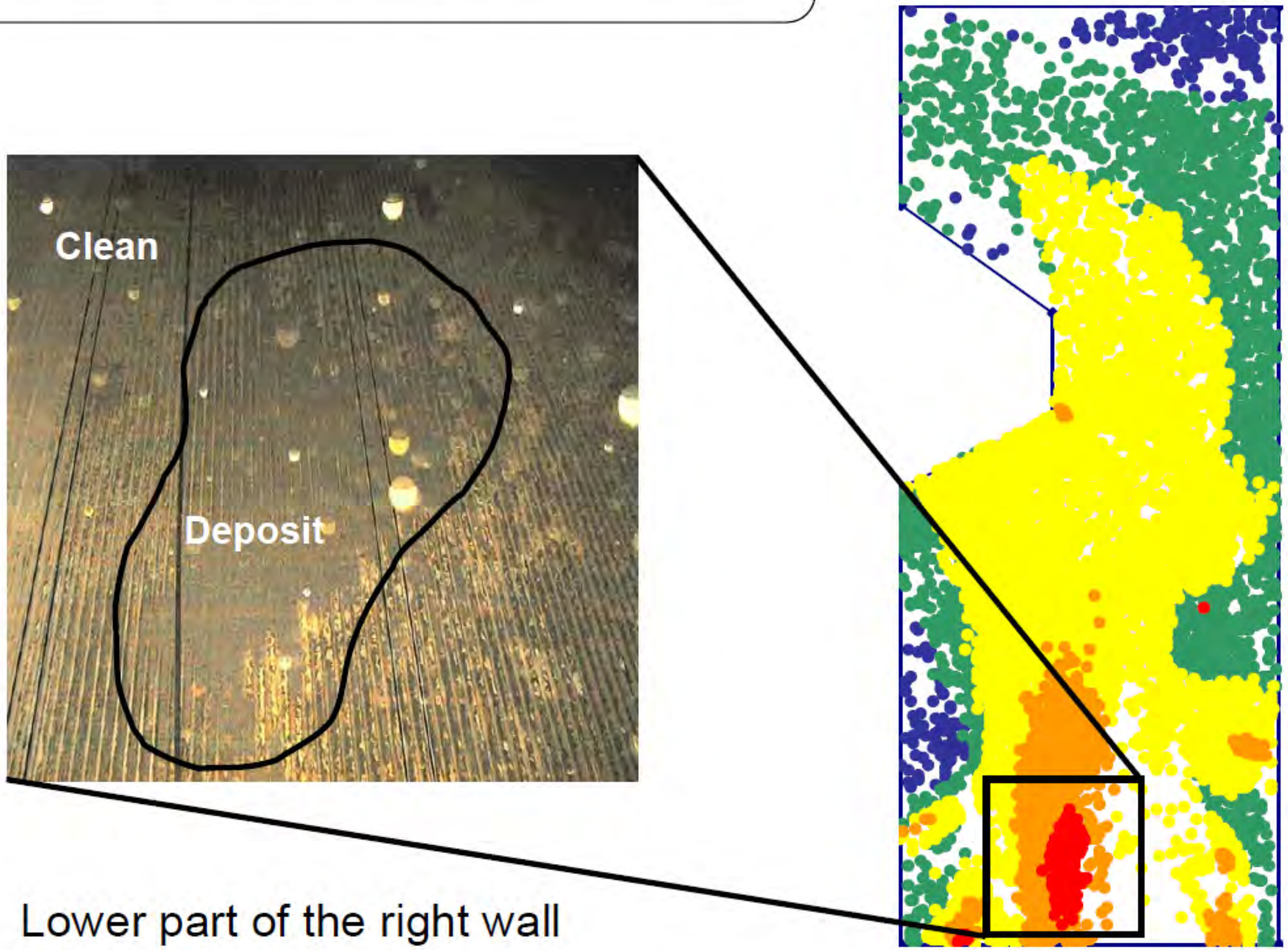
731-733 °C

Example for biomass boilers



Mueller, Skrifvars, Backman, Hupa (2003) in ”Progress in CFD”

Visual Validation of Deposition Model



Lower part of the right wall

Peat

More of Gunnar's contributions to combustion applications

Energy & Fuels **2006**, *20*, 359–363

Influence of Black Liquor Variability, Combustion, and Gasification Process Variables and Inaccuracies in Thermochemical Data on Equilibrium Modeling Results

Anders Larsson,* Anders Nordin, Rainer Backman, and Björn Warnqvist

Energy Technology and Thermal Process Chemistry, Umeå University, SE-90187 Umeå, Sweden

Gunnar Eriksson

GTT-Technologies, Kaiserstrasse 100, D-52134 Herzogenrath, Germany

Environ. Sci. Technol. **2001**, *35*, 1867–1874

Thermodynamic Modeling of PCDD/Fs Formation in Thermal Processes

PENGFU TAN,[†] IÑAKI HURTADO, AND DIETER NEUSCHÜTZ

Lehrstuhl für Theoretische Hüttenkunde, Rheinisch–Westfälische Technische Hochschule Aachen, Korpernikusstrasse 16, D-52056 Aachen, Germany

GUNNAR ERIKSSON

GTT-Technologies, Kaiserstrasse 100, 52134 Herzogenrath, Germany

Environ. Sci. Technol. **1996**, *30*, 50–56

Thermodynamic Behavior of Metal Chlorides and Sulfates under the Conditions of Incineration Furnaces

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Department of Industrial Chemistry, Free University of Brussels (VUB), Pleinlaan 2, 1050 Brussels, Belgium

PHILIP J. SPENCER AND GUNNAR ERIKSSON

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Thermodynamic modeling of ash chemistry in combustion

- Useful tool for modeling alkali salt melting and reactions in BL recovery boilers
  - Bed behavior, corrosion, deposit formation
- Useful tool for predicting ash chemistry in biomass and coal combustion
  - Well-defined databases for coal ashes and slags
  - Database for salt phases including Ca, Mg, Pb, Zn, and P is being developed
  - Databases for alkali-rich silicates need development
  - Limitations of kinetics, fuel speciation, combustion techniques need to be addressed for proper use of thermodynamic modeling

Gratulerar Gunnar

önskar

alla vänner vid

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