Chemical thermodynamics in industrial processes

Thermodynamic Modeling of Combustion Processes – Applications and Limitations

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Åbo Akademi
Combustion and Materials Research

ICG –TC3: School Thermodynamic of Glass
Erlangen, Germany, 12.5.2019

Combustion and materials research

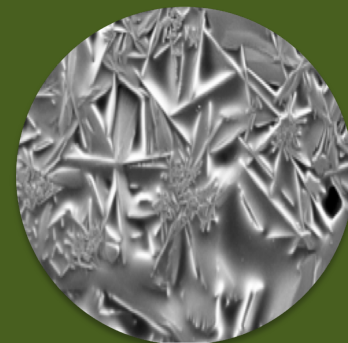
chemistry of high-temperature processes
properties of high-temperature materials

Biomass combustion

- Biomass characterization
- Thermal conversion of fuel particles
- Emissions
- High temperature corrosion and erosion

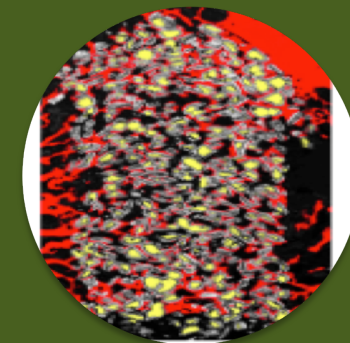
Circular economy

- Refining of metals from ashes and sludges
- Utilization of sidestreams as raw materials
- Material interactions



Ceramics and glasses

- Glazes on sanitaryware and ceramic tiles
- Functional coatings
- Tableware glasses
- Mineral wool
- Concrete

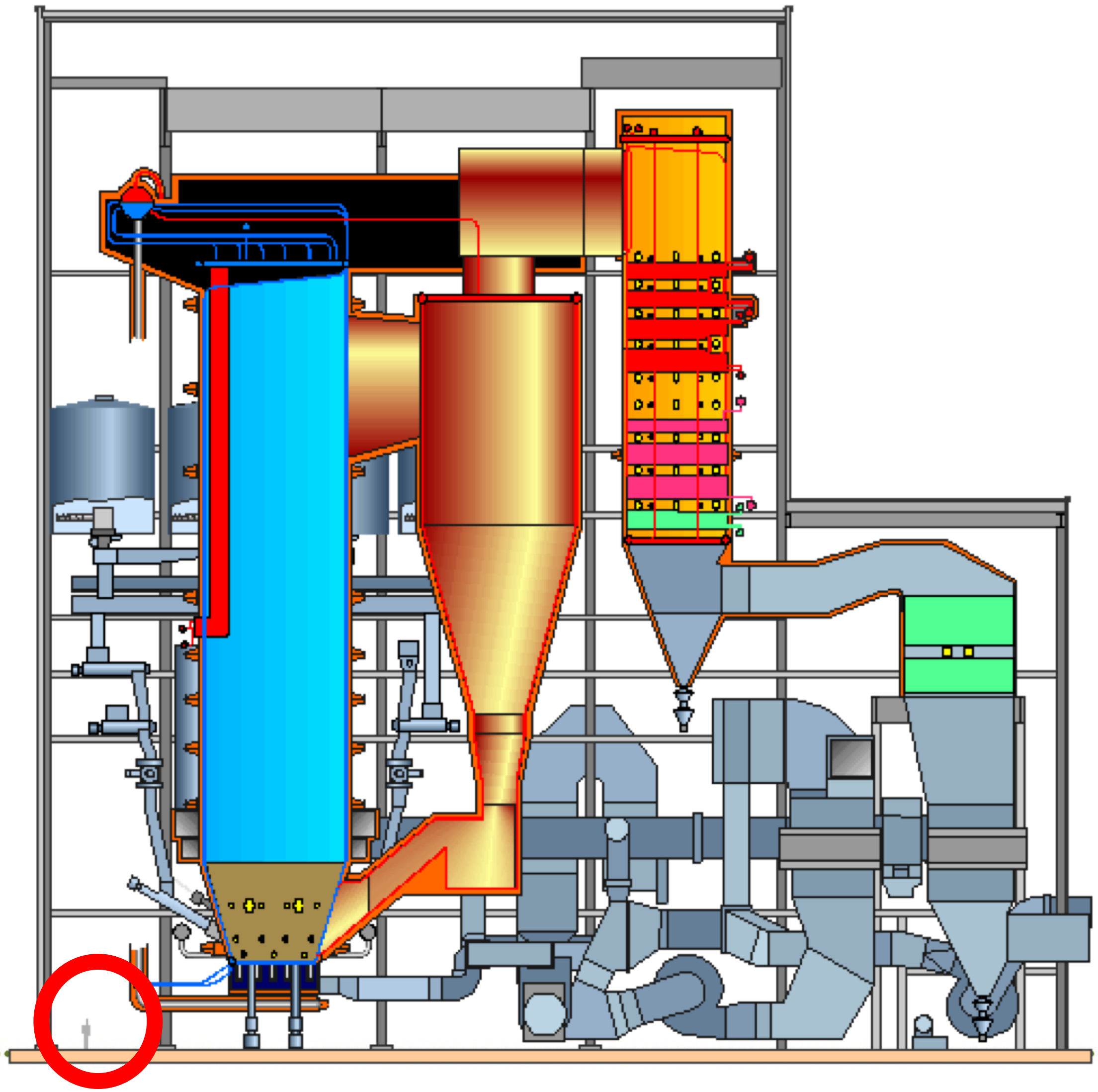


Biomedical materials

- Bioactive glasses
- Bioactive glass - biopolymer composites
- Tissue engineering scaffolds
- Dissolution behaviour in body environment

inorganic materials and high-temperature processes

Circulating fluidized bed combustion



Alholmen CFBC
Jakobstad, Finland

550 MW (545 ° C)

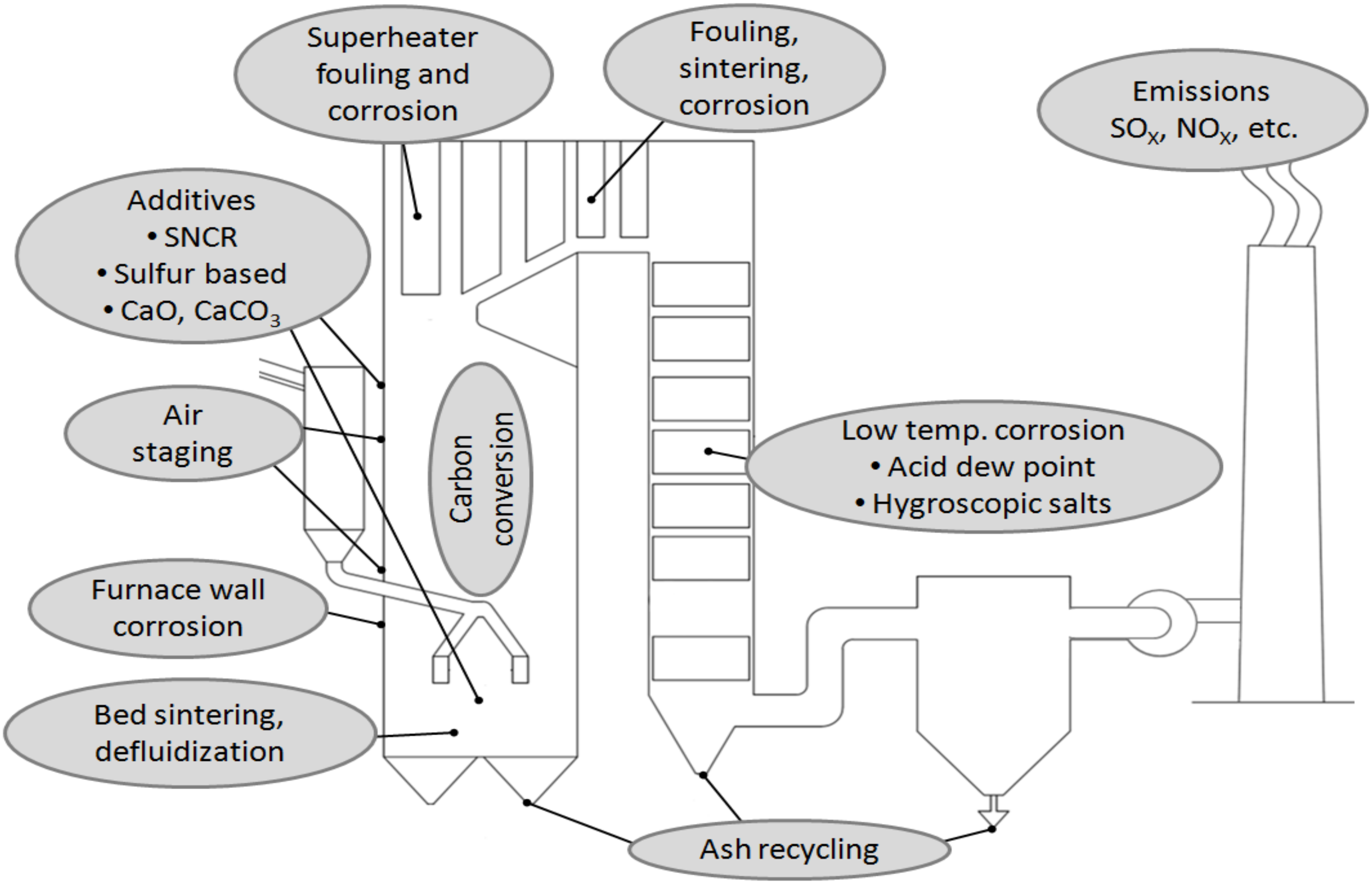
Peat, Bark, REF, Forest Residue, Sawdust, Coal, Oil

Boiler Efficiency 92 %

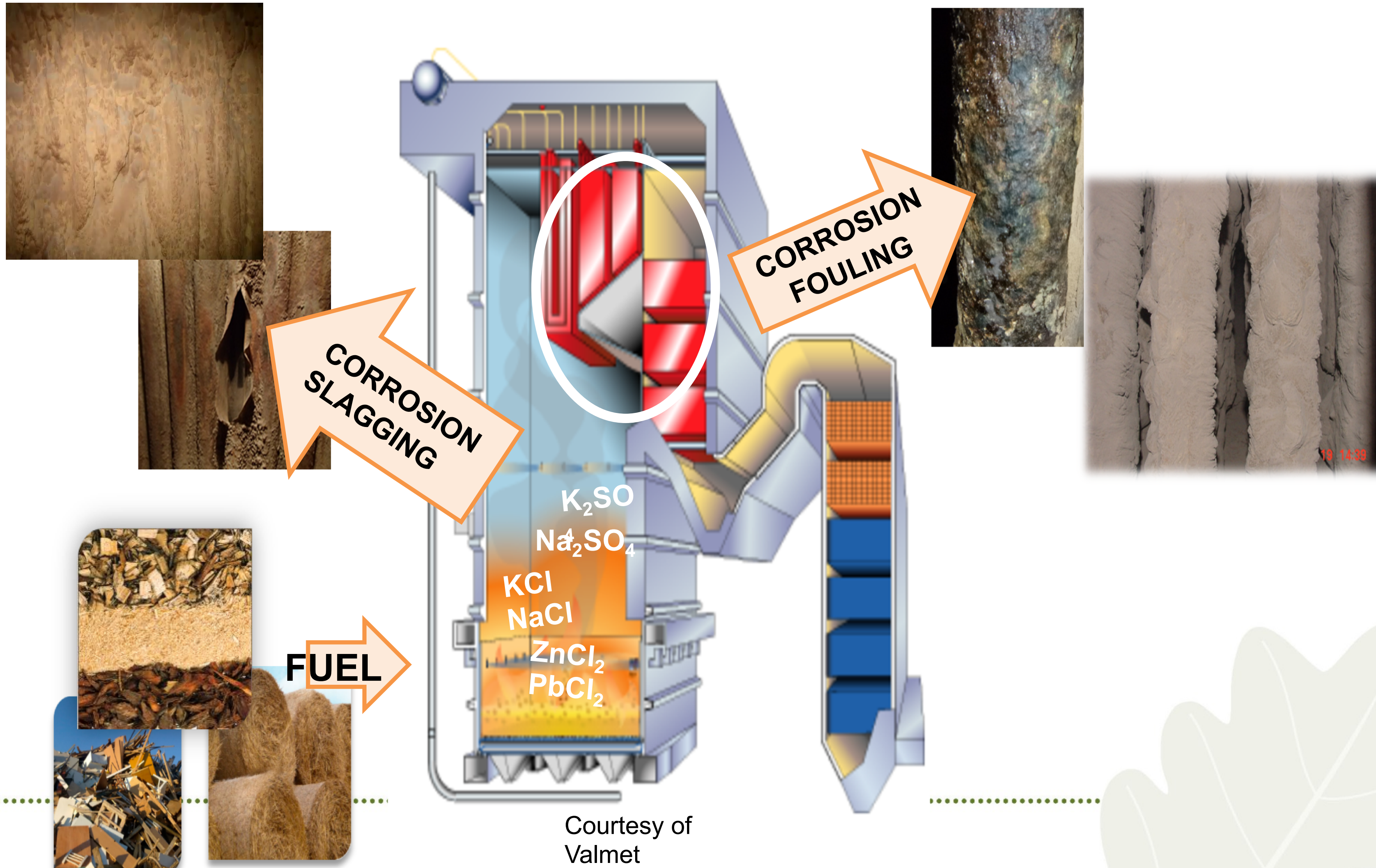
NO_x 50 mg/MJ
SO_2 100 mg/MJ
Particulate 30 mg/m^3n

Courtesy of Valmet

Challenges in Biomass and Waste Combustion - chemical details

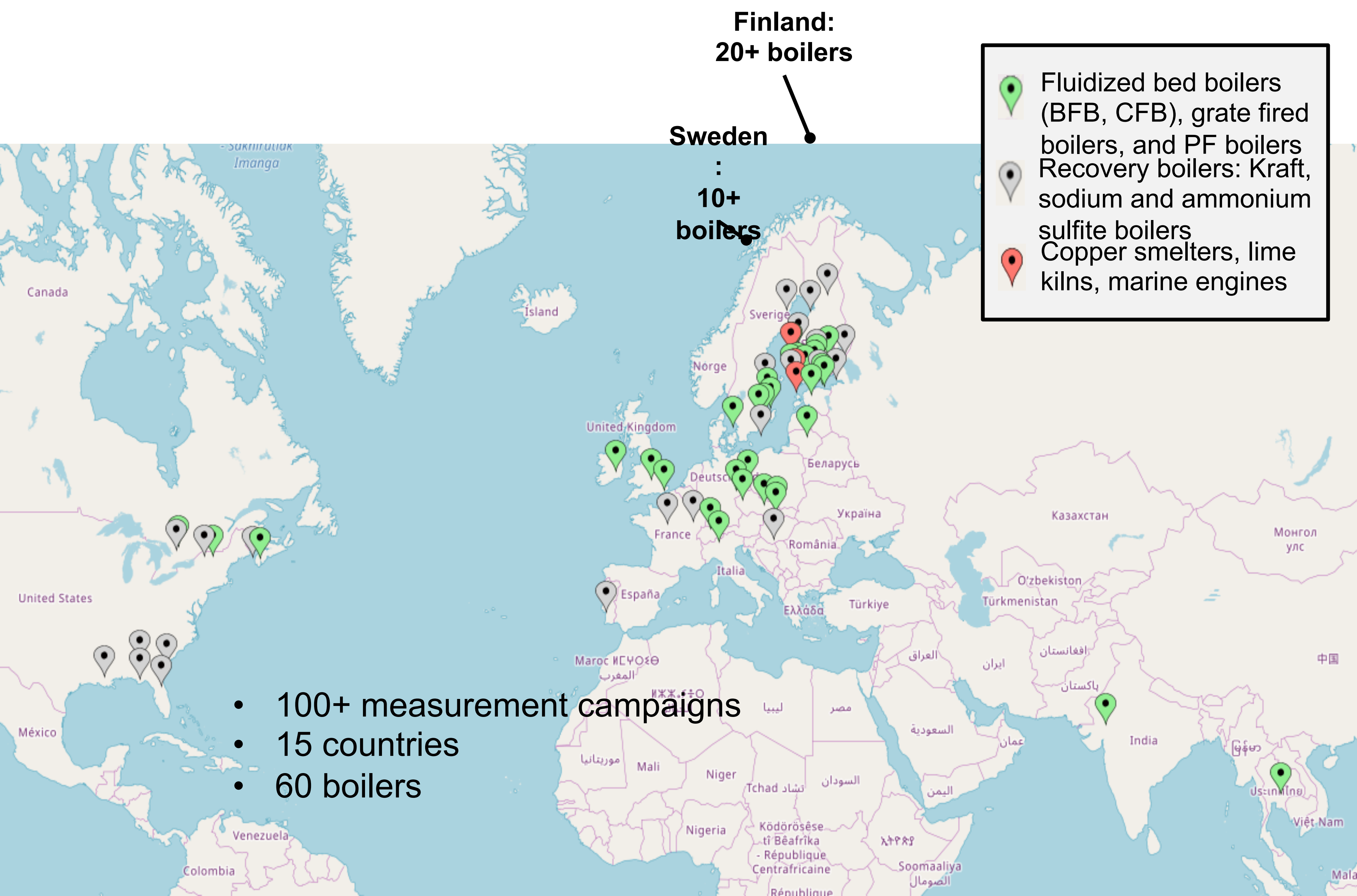


Fluidized bed combustion – ash related challenges



Courtesy of Valmet

Åbo Akademi measurement campaigns



- 100+ measurement campaigns
- 15 countries
- 60 boilers

Equilibrium Calculations in Combustion Systems

- Gaseous Combustion Equilibria
- Solid-Gas Equilibria
- Equilibria with a Molten Phase
- Equilibria and NOx

Equilibrium Calculations in Combustion Systems

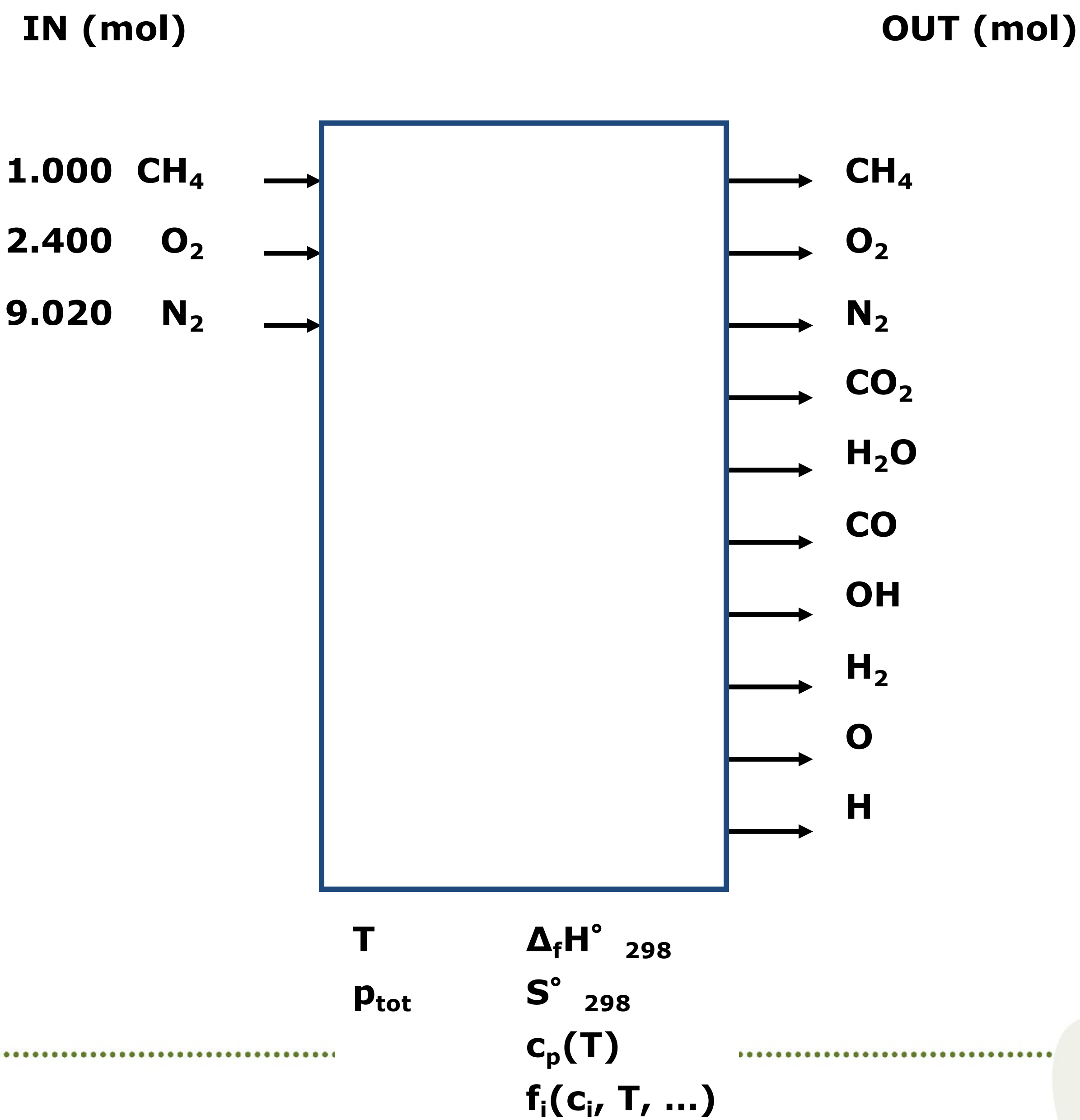
- **Gaseous Combustion Equilibria**
- Solid-Gas Equilibria
- Equilibria with a Molten Phase
- Equilibria and NOx

Gaseous Combustion Equilibria:

Methane combustion as a function of lambda

Stoichiometric reaction:

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$



IN (mol)
OUT (mol)
1.000 CH_4
2.400 O_2
9.020 N_2
CH_4
O_2
N_2
CO_2
H_2O
CO
OH
H_2
O
H
T
p_{tot}
$\Delta_f H^\circ_{298}$
S°_{298}
$c_p(T)$
$f_i(c_i, T, \ldots)$

T = 1623.00 K
P = 1.01325E+00 bar

	Input amount (mol)	Equil. amount (mol)	Equil. pressure (bar)
CH_4	0.10000E+01	0.28810E−14	0.23503E−15
O_2	**0.24000E+01**	**0.39950E+00**	0.32590E−01
N_2	**0.90200E+01**	**0.90200E+01**	0.73583E+00
CO_2	0.00000E+00	**0.99985E+00**	0.81565E−01
H_2O	0.00000E+00	**0.19987E+01**	0.16305E+00
CO	**0.00000E+00**	**0.15127E−03**	0.12340E−04
OH	0.00000E+00	0.24237E−02	0.19772E−03
H_2	0.00000E+00	0.95625E−04	0.78008E−05
O	0.00000E+00	0.42256E−04	0.34472E−05
H	0.00000E+00	0.23646E−05	0.19290E−06

IN (mol)			OUT (mol)	
1.000	CH_4	→ →	CH_4	$3\cdot10^{-15}$
2.400	O_2	→ →	O_2	0.400
9.020	N_2	→ →	N_2	9.020
		→	CO_2	0.999
		→	H_2O	1.999
		→	CO	$2\cdot10^{-4}$
		→	OH	0.002
		→	H_2	$1\cdot10^{-4}$
		→	O	$4\cdot10^{-5}$
		→	H	$2\cdot10^{-6}$

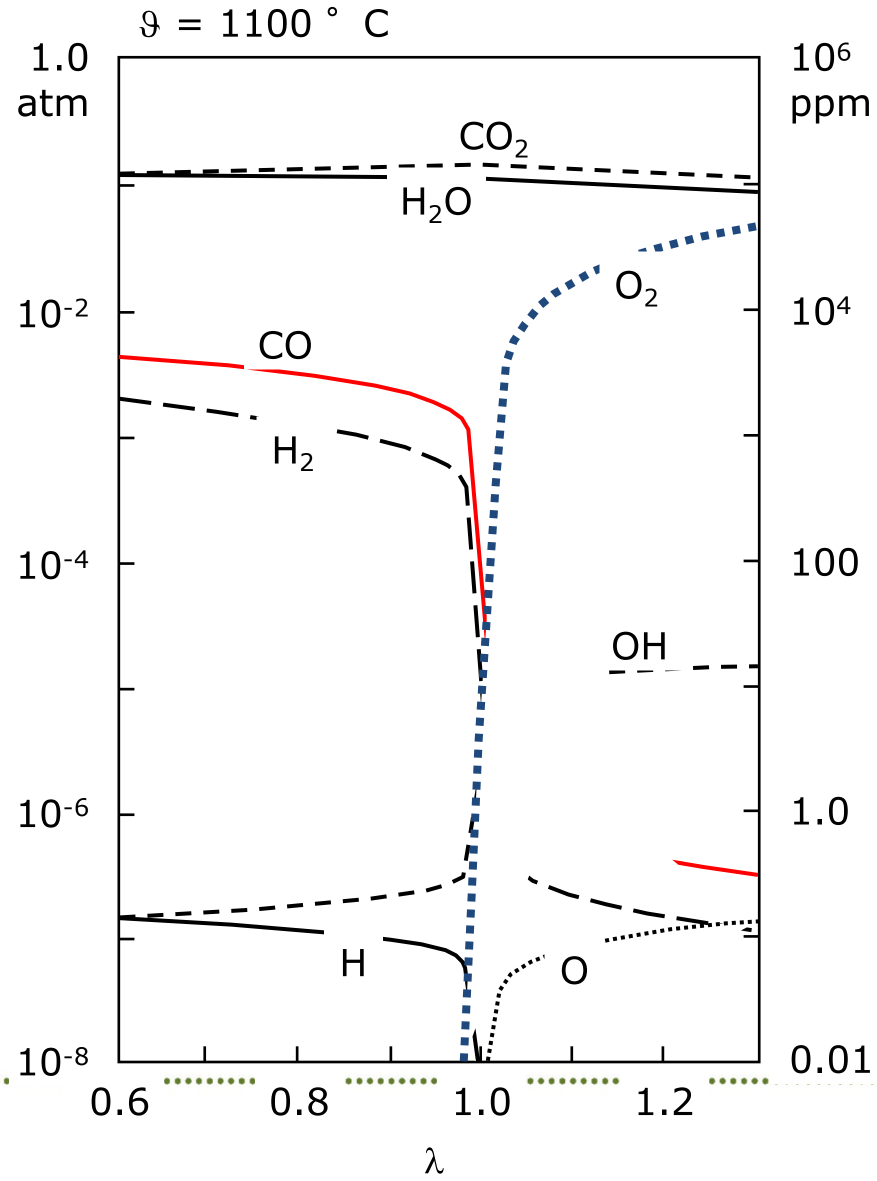
T — $\Delta_f H^\circ_{298}$

p_{tot} — S°_{298}

$c_p(T)$

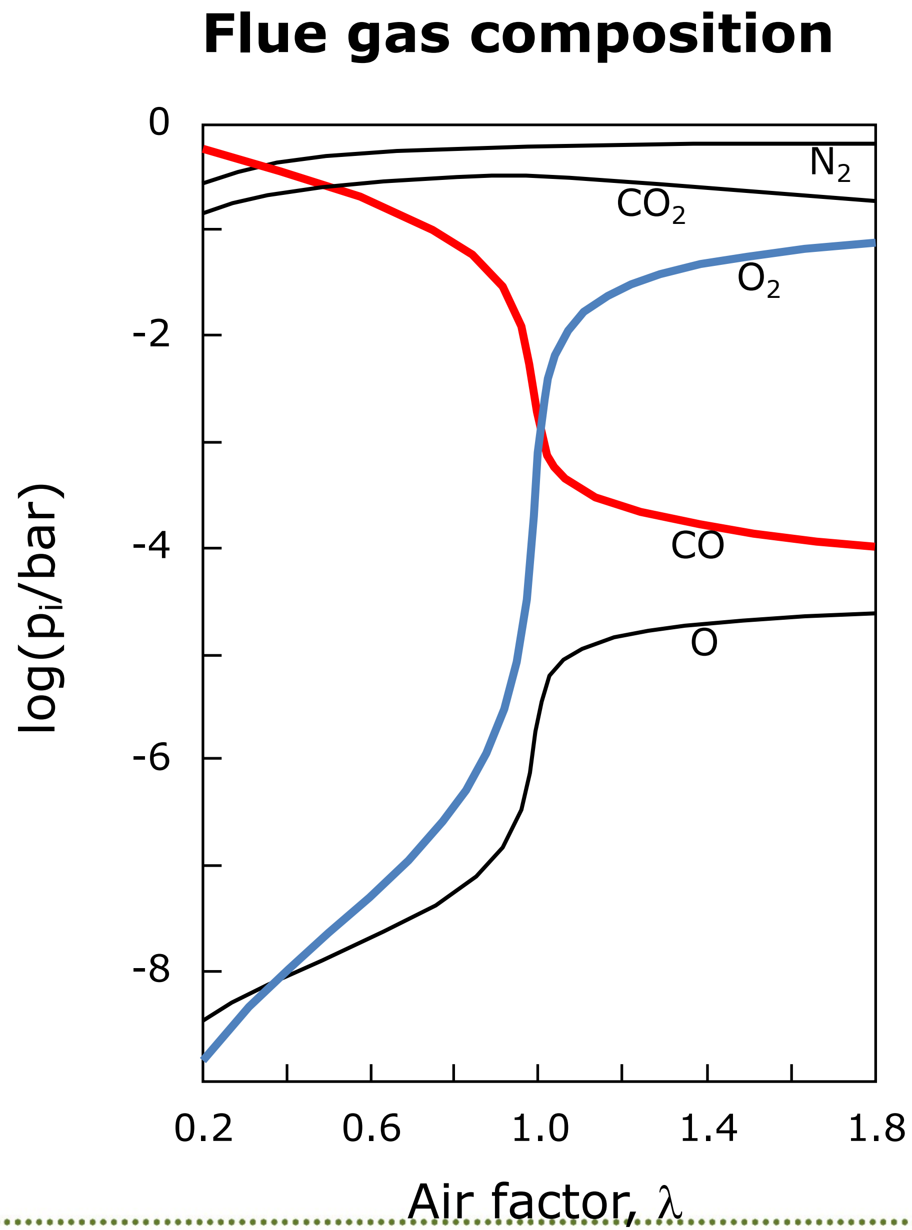
$f_i(c_i, T, \ldots)$

Methane/Air Combustion Equilibrium as a Function of Air Factor (at 1100 C)



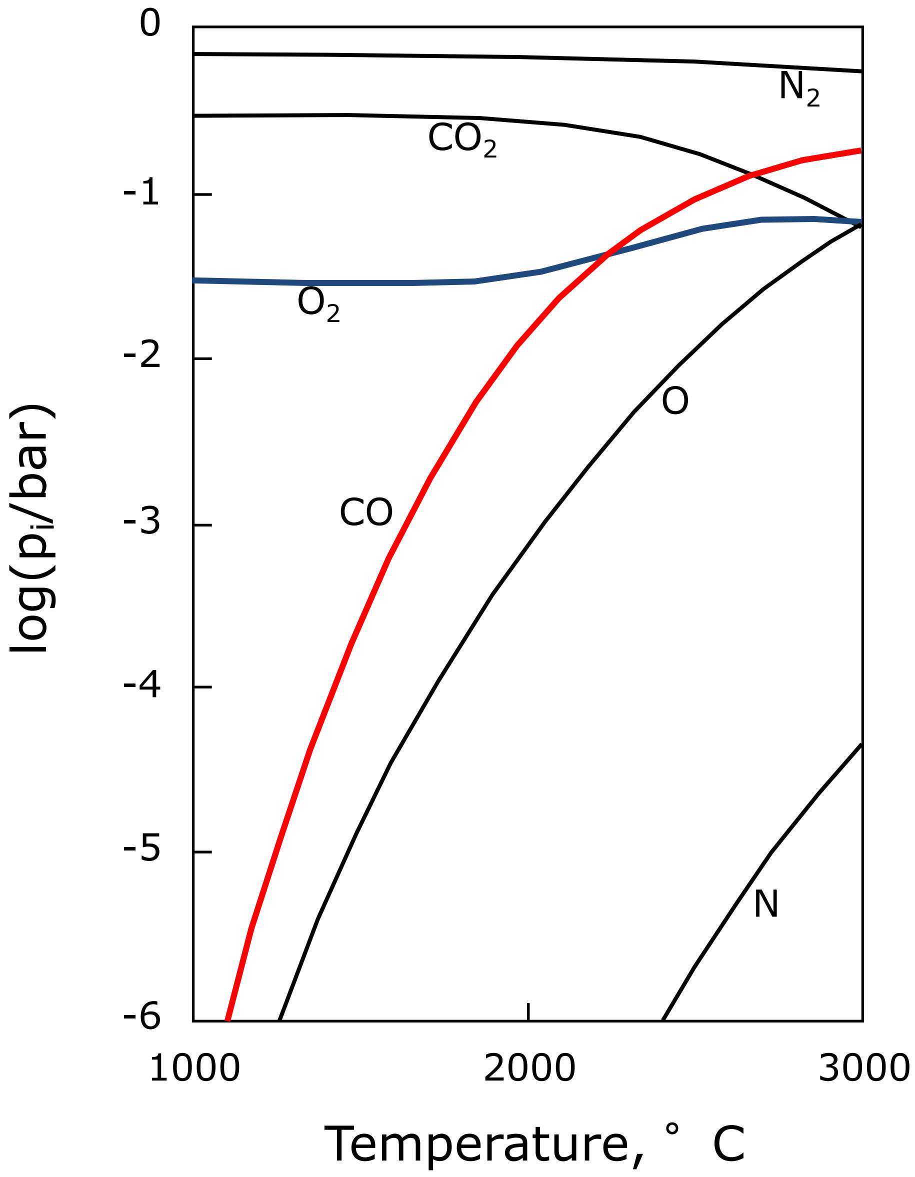
Gaseous Combustion Equilibria

Energy balance and adiabatic combustion temperature

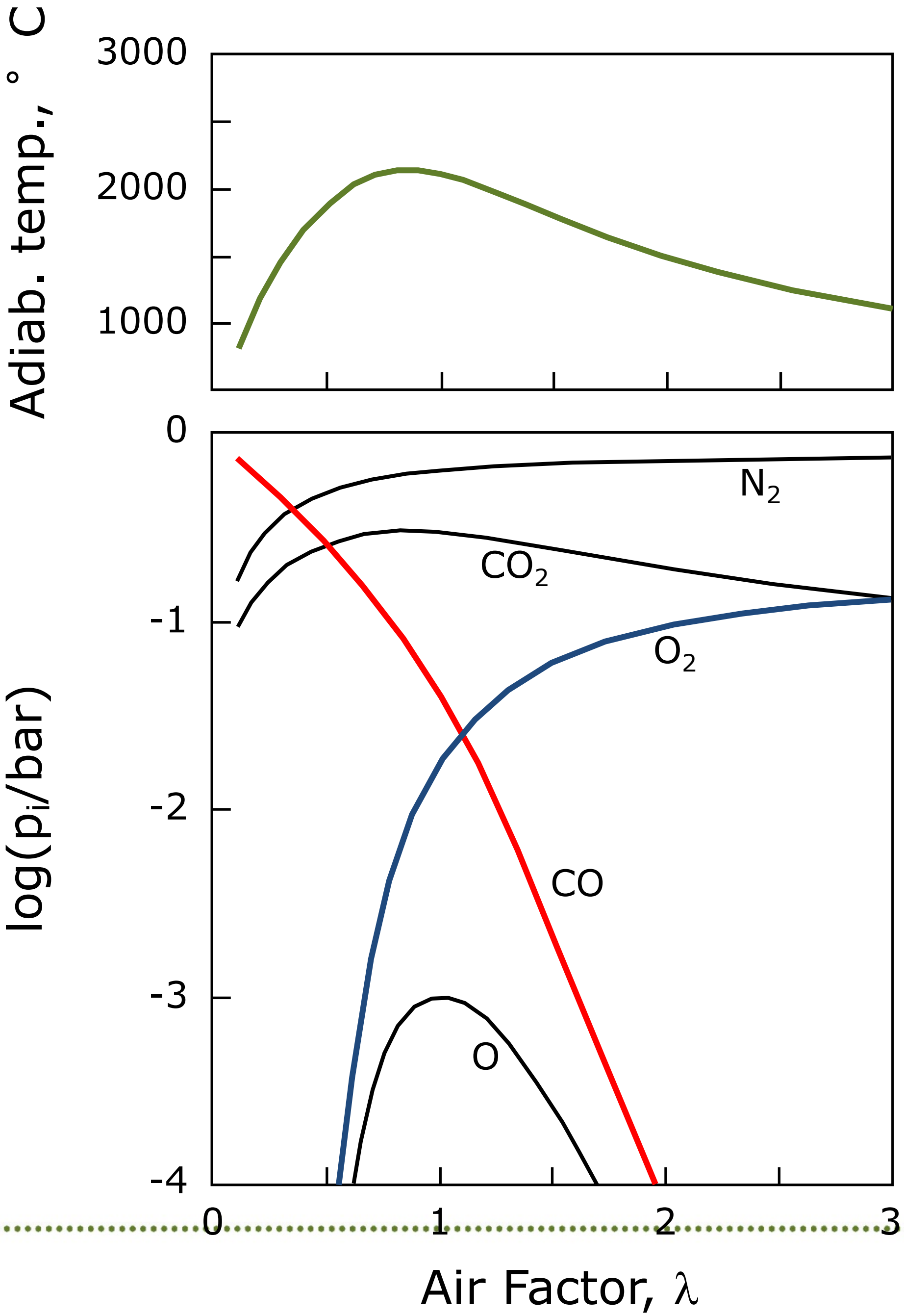


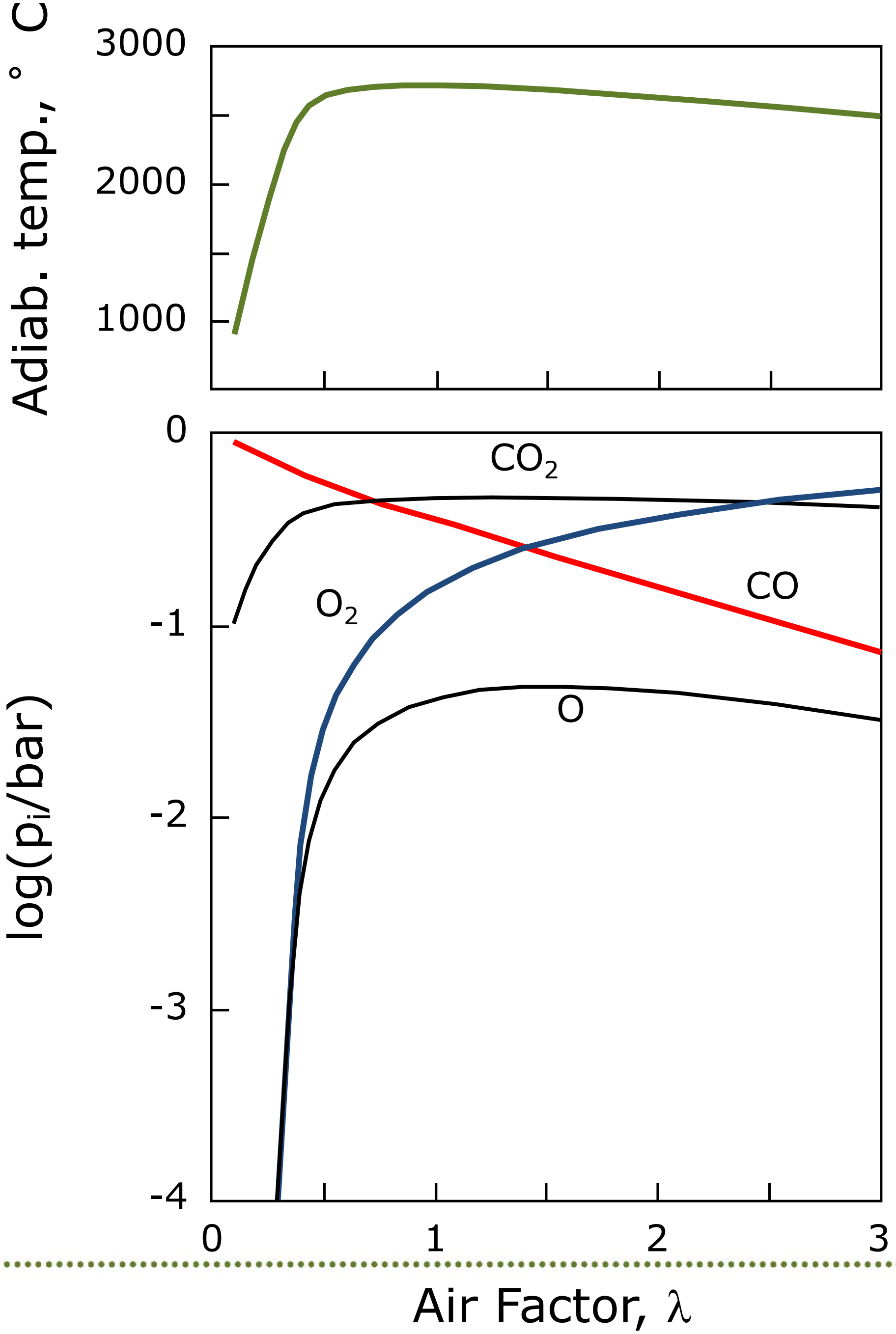
Equilibrium in Combustion of CO vs. Air Factor (1500 ^{o}C)

Equilibrium in Combustion of CO vs. Temperature (λ = 1.2)



Equilibrium in Combustion of CO with **Air** – Adiabatic Temperature vs. Air Factor



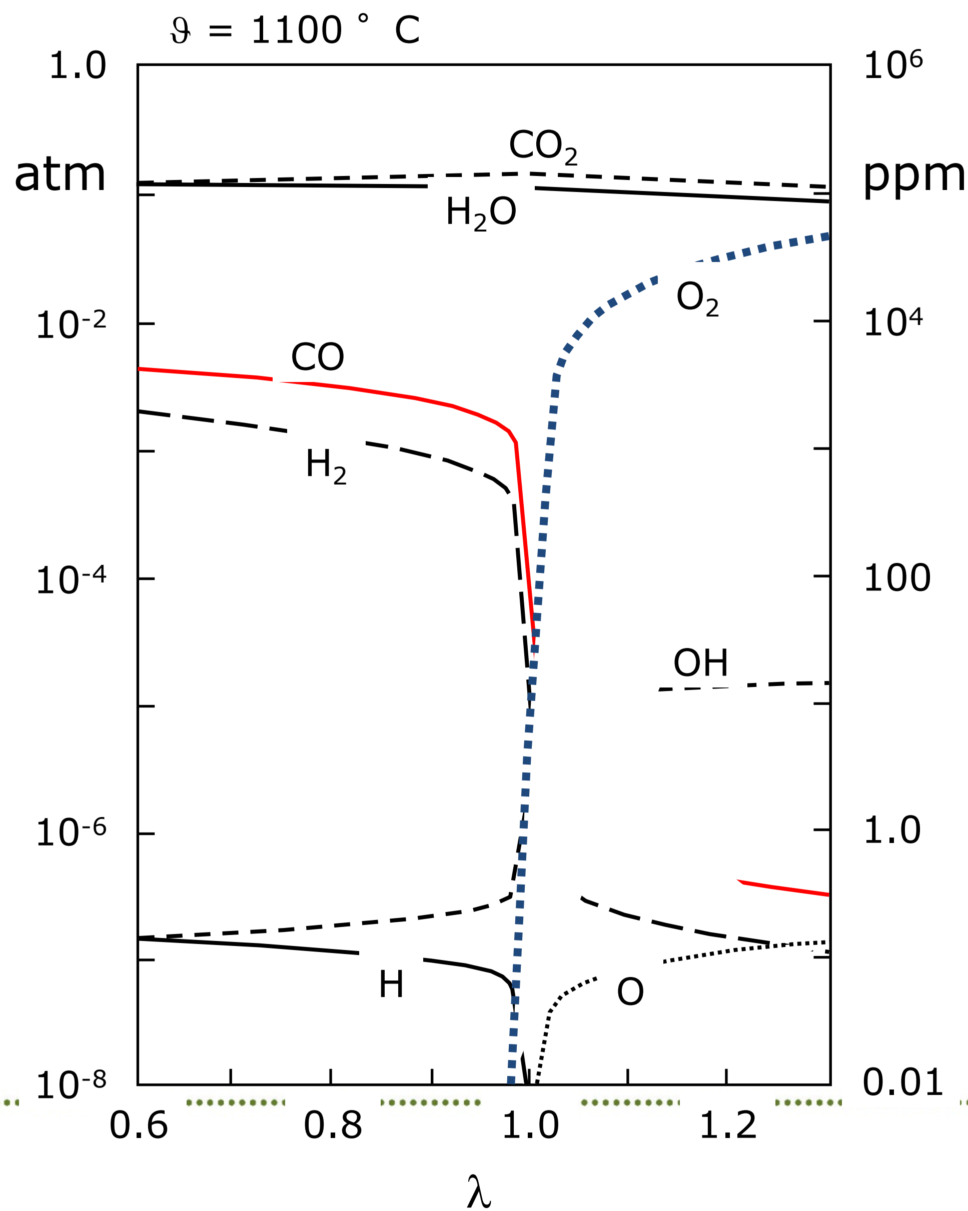


Equilibrium in Combustion of CO with **Oxygen** – Adiabatic Temperature vs. Lambda

Gaseous combustion:

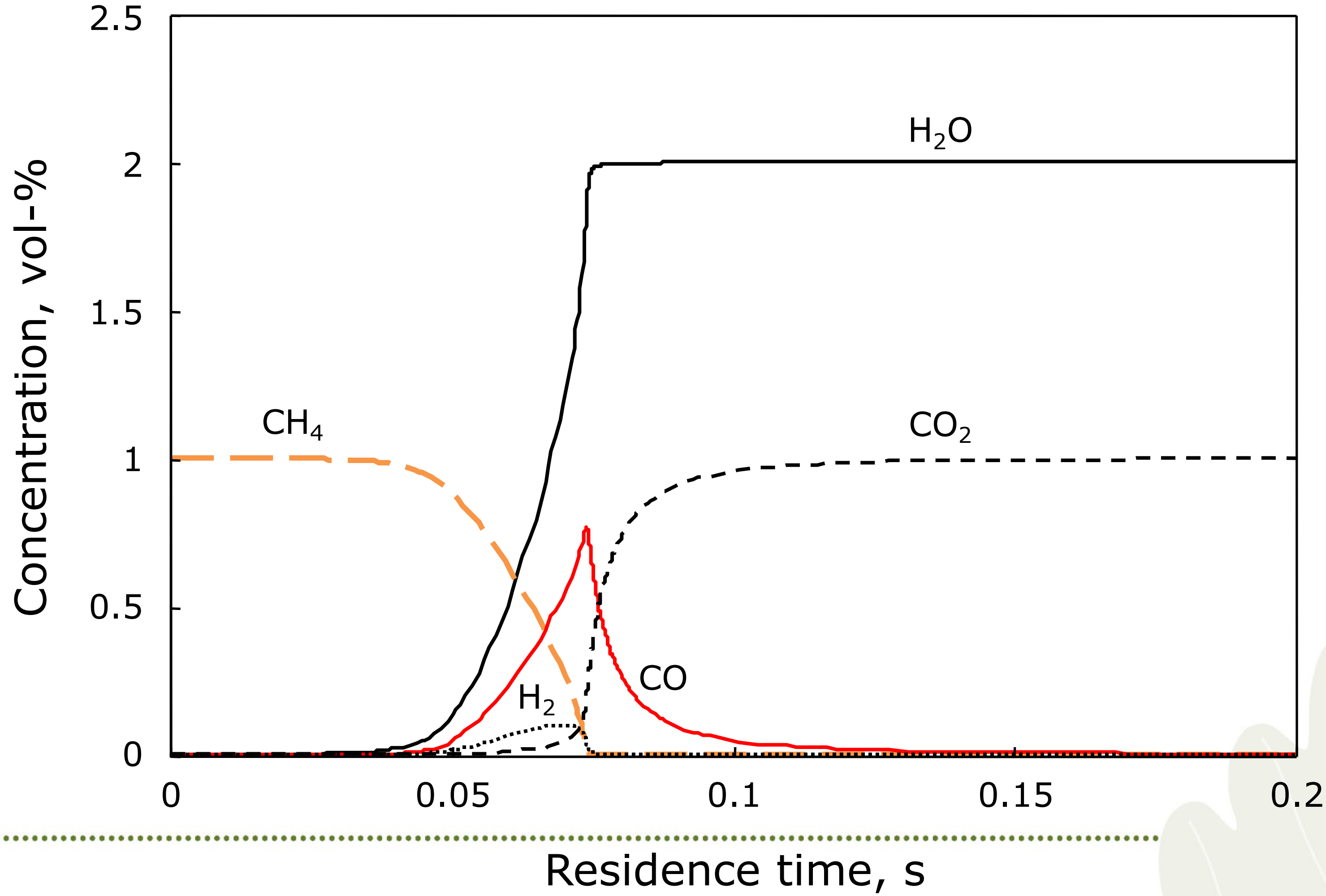
How ”true” is the equilibrium assumption?

Methane/Air Combustion Equilibrium as a Function of Air Factor (at 1100 ° C)



Combustion of methane (1 vol-%) with air, 850 °C
Kinetic model calculation.

Stoichiometric reaction: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$



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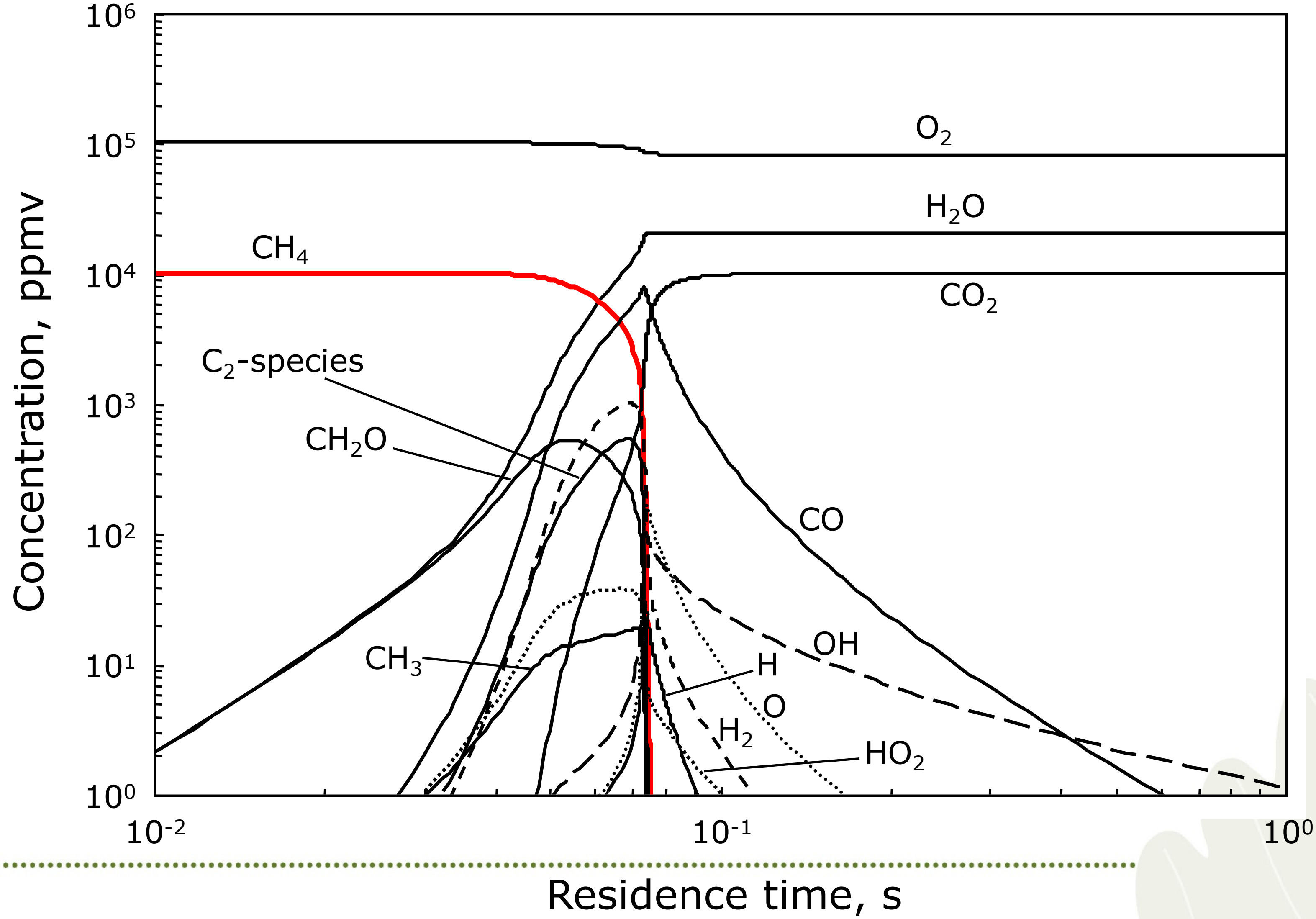


Gaseous combustion:

How ”true” is the equilibrium assumption?

Typical time to equilibrium:

For T = 850 ° C, time = 0.05 - 1 s

For T=1500 ° C, time = 1 – 10 ms

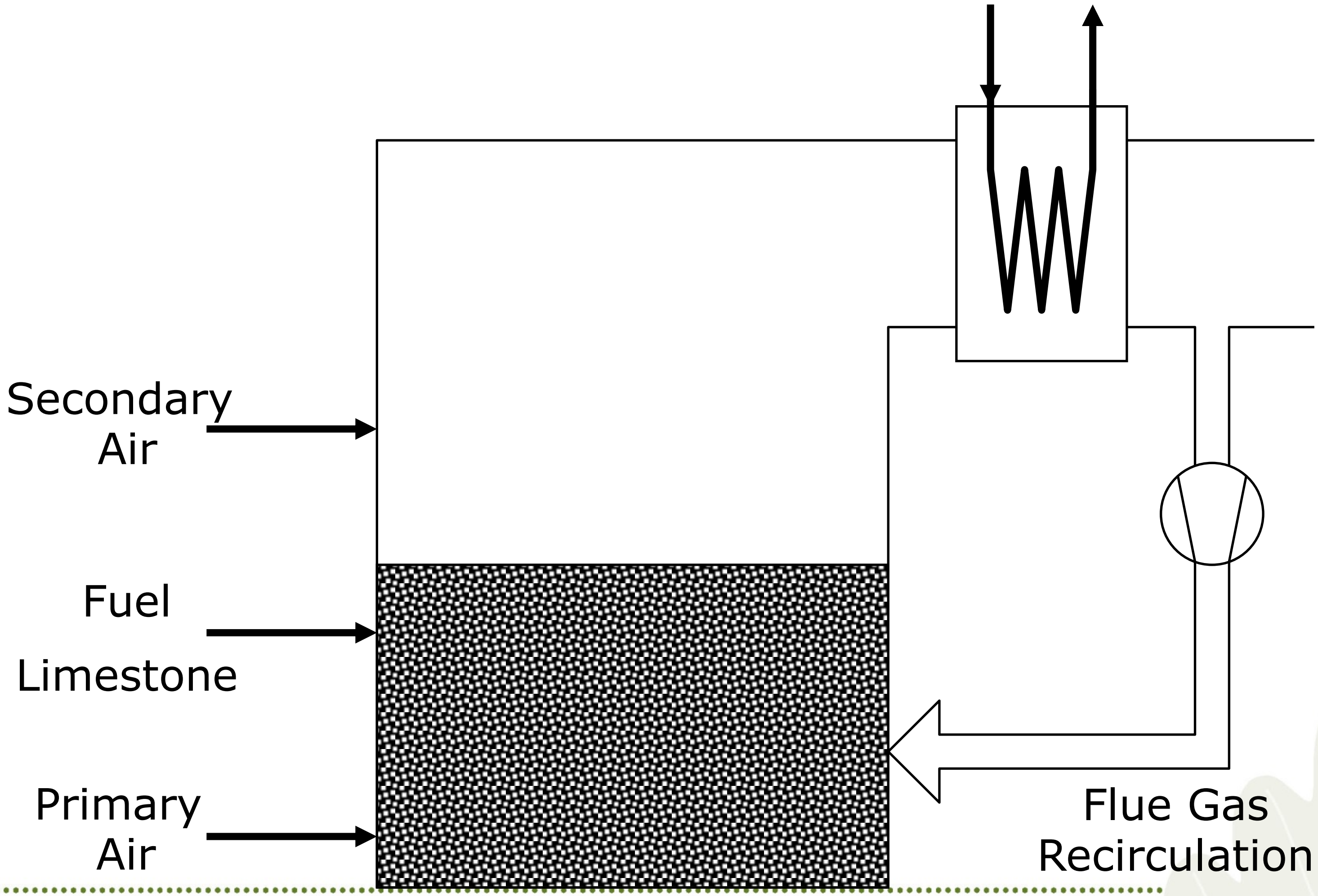
Equilibrium Calculations in Combustion Systems

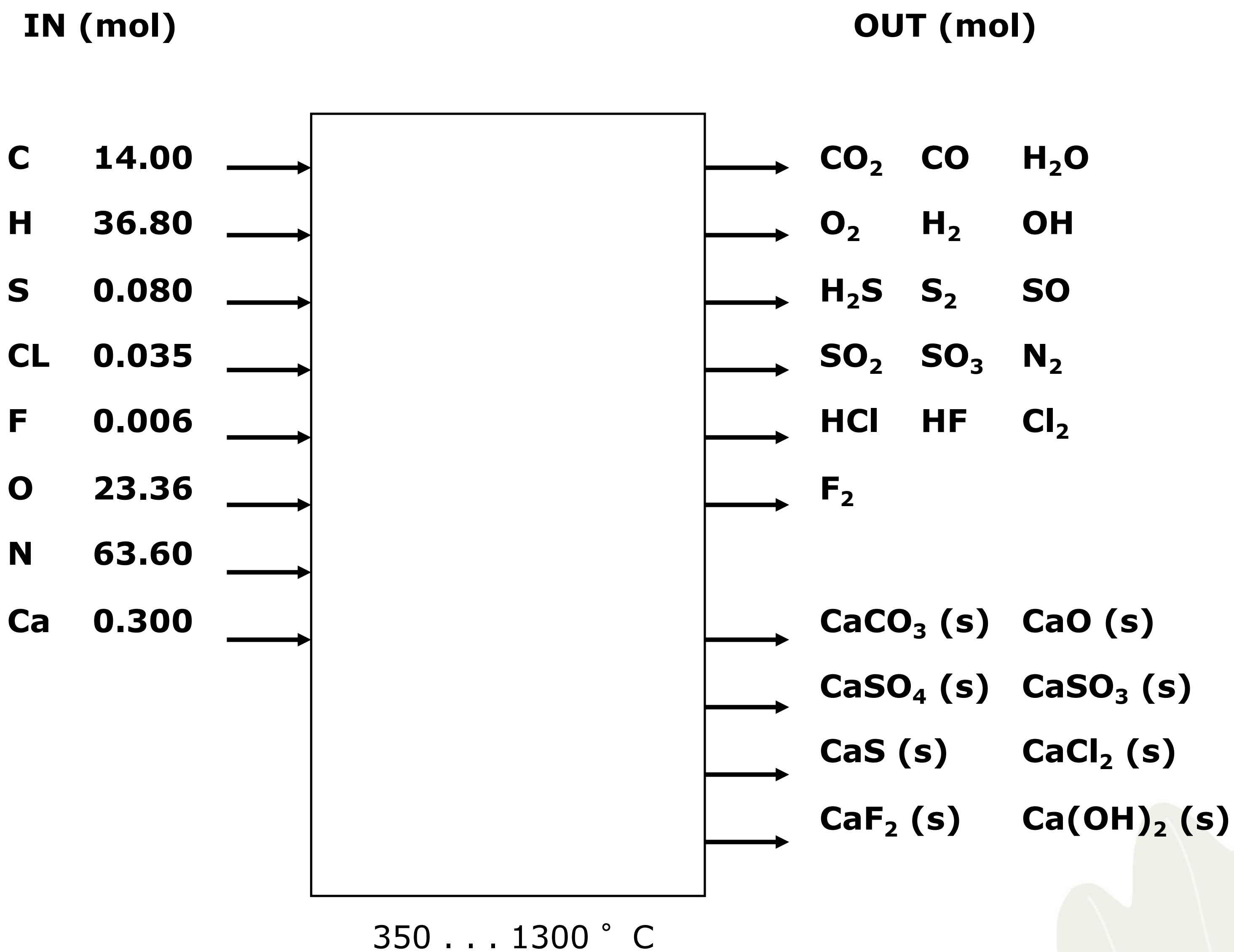
- Gaseous Combustion Equilibria
- **Solid-Gas Equilibria**
- Equilibria with a Molten Phase
- Equilibria and NOx

Solid-Gas Equilibria:

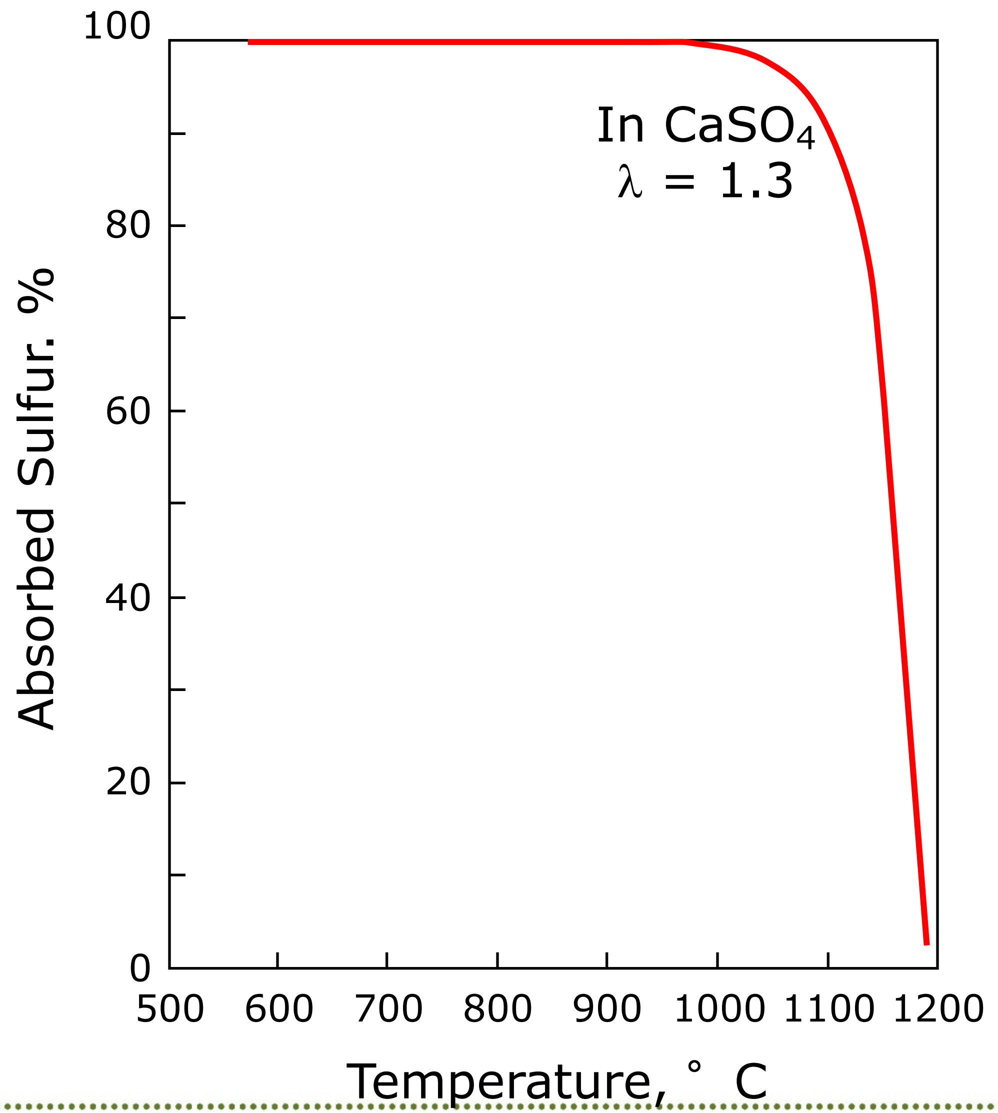
Capture of SO_2, HCl, HF by Limestone

Bubbling Fluidized Bed Combustion with Limestone Addition

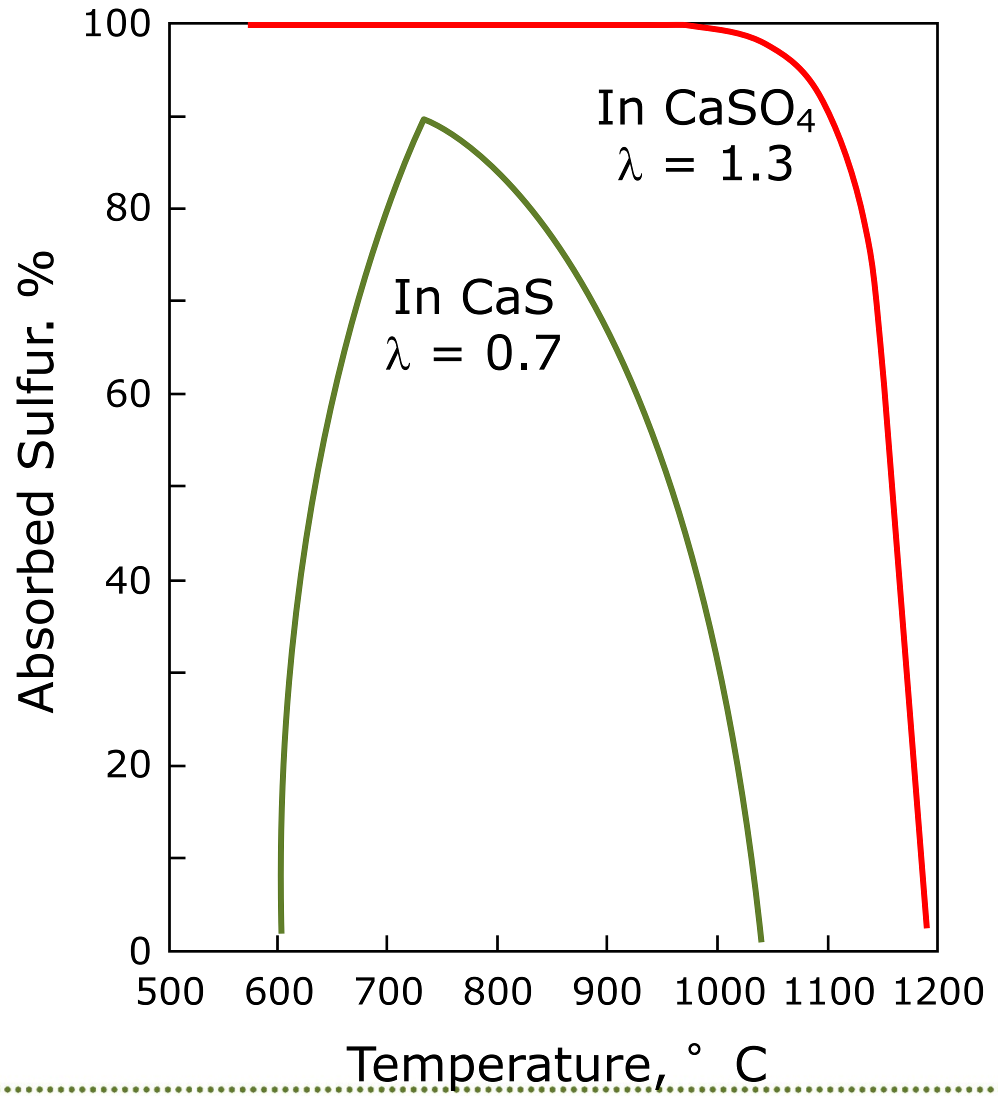



IN (mol)
OUT (mol)
C 14.00
H 36.80
S 0.080
CL 0.035
F 0.006
O 23.36
N 63.60
Ca 0.300
CO_2 CO H_2O
O_2 H_2 OH
H_2S S_2 SO
SO_2 SO_3 N_2
HCl HF Cl_2
F_2
$CaCO_3$ (s) CaO (s)
$CaSO_4$ (s) $CaSO_3$ (s)
CaS (s) $CaCl_2$ (s)
CaF_2 (s) $Ca(OH)_2$ (s)
350 . . . 1300 ° C

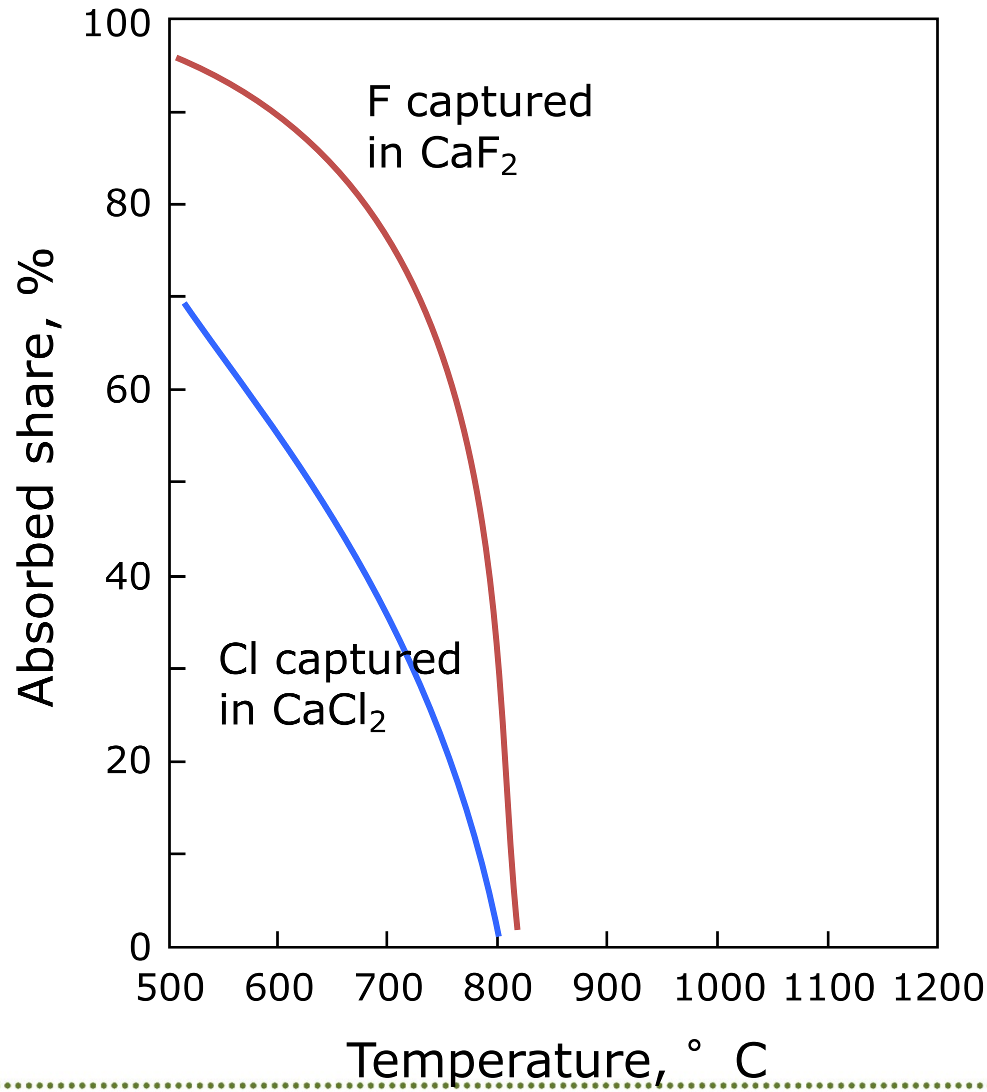
Sulfur Captured in $CaSO_4$ at λ = 1.3



Sulfur Captured in $CaSO_4$ at $\lambda = 1.3$, and in CaS at $\lambda = 0.7$



Captured HCl and HF vs. Temperature ($\lambda = 0.7$)



The Impact of Temperature on SO_2, HCl and HF Capture with Limestone Addition

	650 ° C mol	650 ° C %-absorption	1050 ° C mol	1050 ° C %-absorption
SO_2 (g) $CaSO_4$ (s)	$6 \cdot 10^{-10}$ 0.080	100.0	0.0017 0.0783	97.9
HCl (g) $CaCl_2$ (s)	0.0346 0.0002	1.2	0.0350 –	0.0
HF (g) CaF_2 (s)	0.0018 0.0021	69.8	0.0060 –	0.0

Summary: solid-Gas Equilibria

- Equilibrium modeling gives boundary conditions to gas reactions
- Equilibrium *percent capture* or *percent solid conversion* case (input) dependent and not generalizable
- Kinetic information needed about solid reactivity and conversion rate

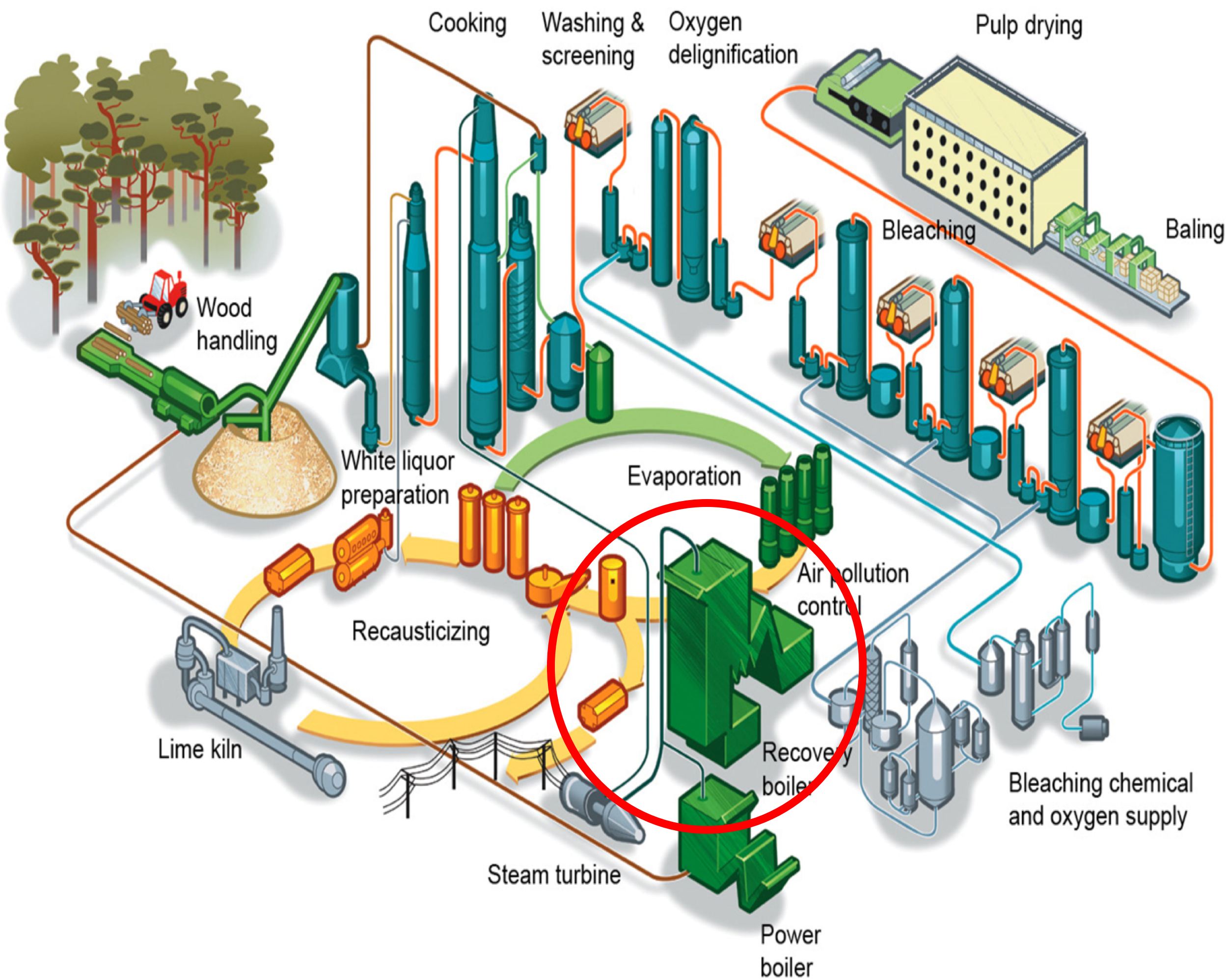
Equilibrium Calculations in Combustion Systems

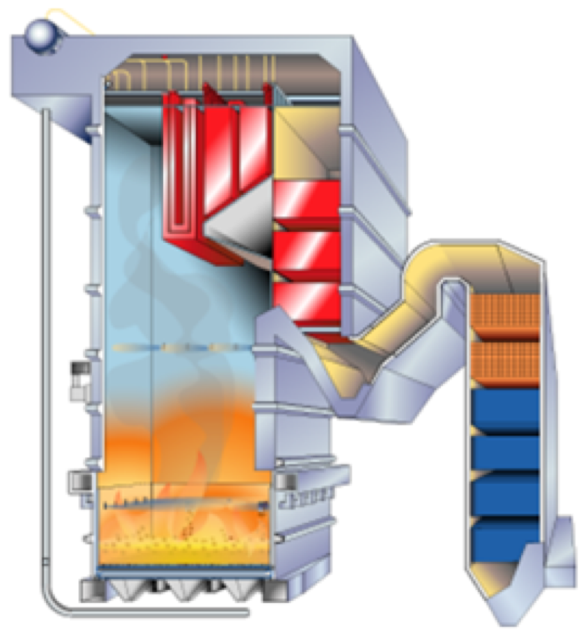
- Gaseous Combustion Equilibria
- Solid-Gas Equilibria
- **Equilibria with a Molten Phase**
- Equilibria and NOx

Equilibria with a Molten Phases:

Black Liquor Recovery Boiler and Alkali Salts

Recovery boiler – a part of chemical pulping process





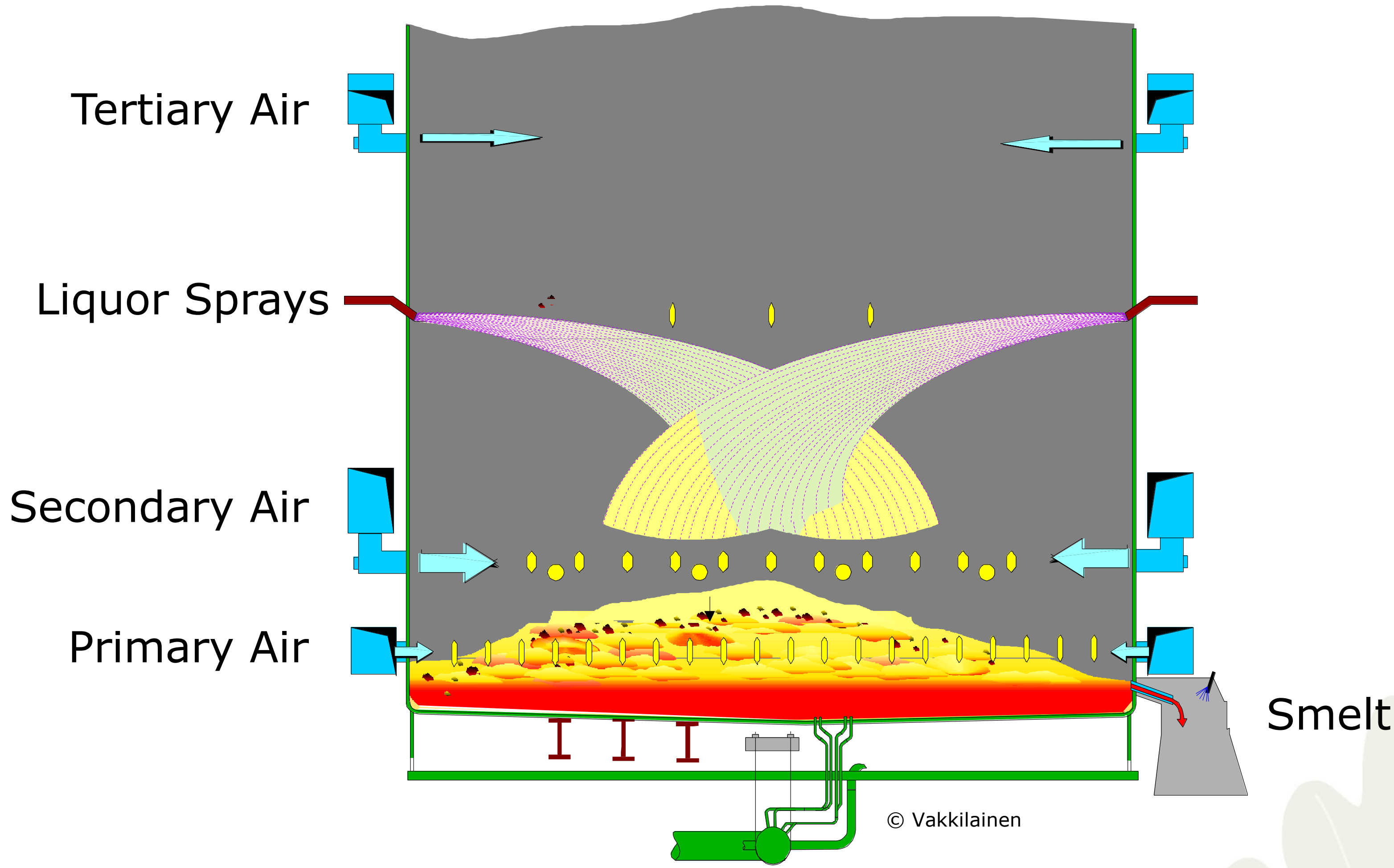
Courtesy of Valmet

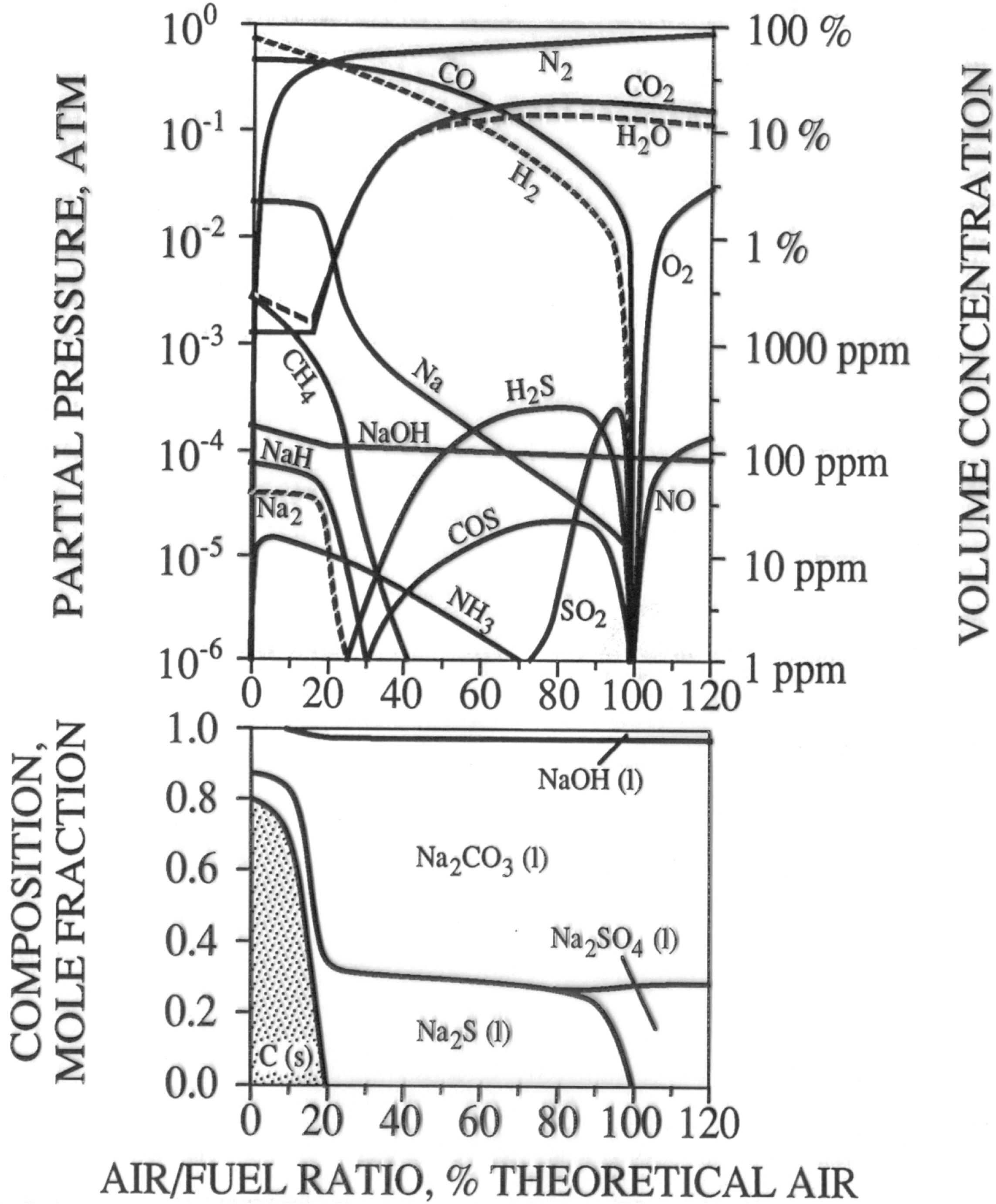
As-Fired Black Liquor Composition

(800 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

Black Liquor Recovery Furnace





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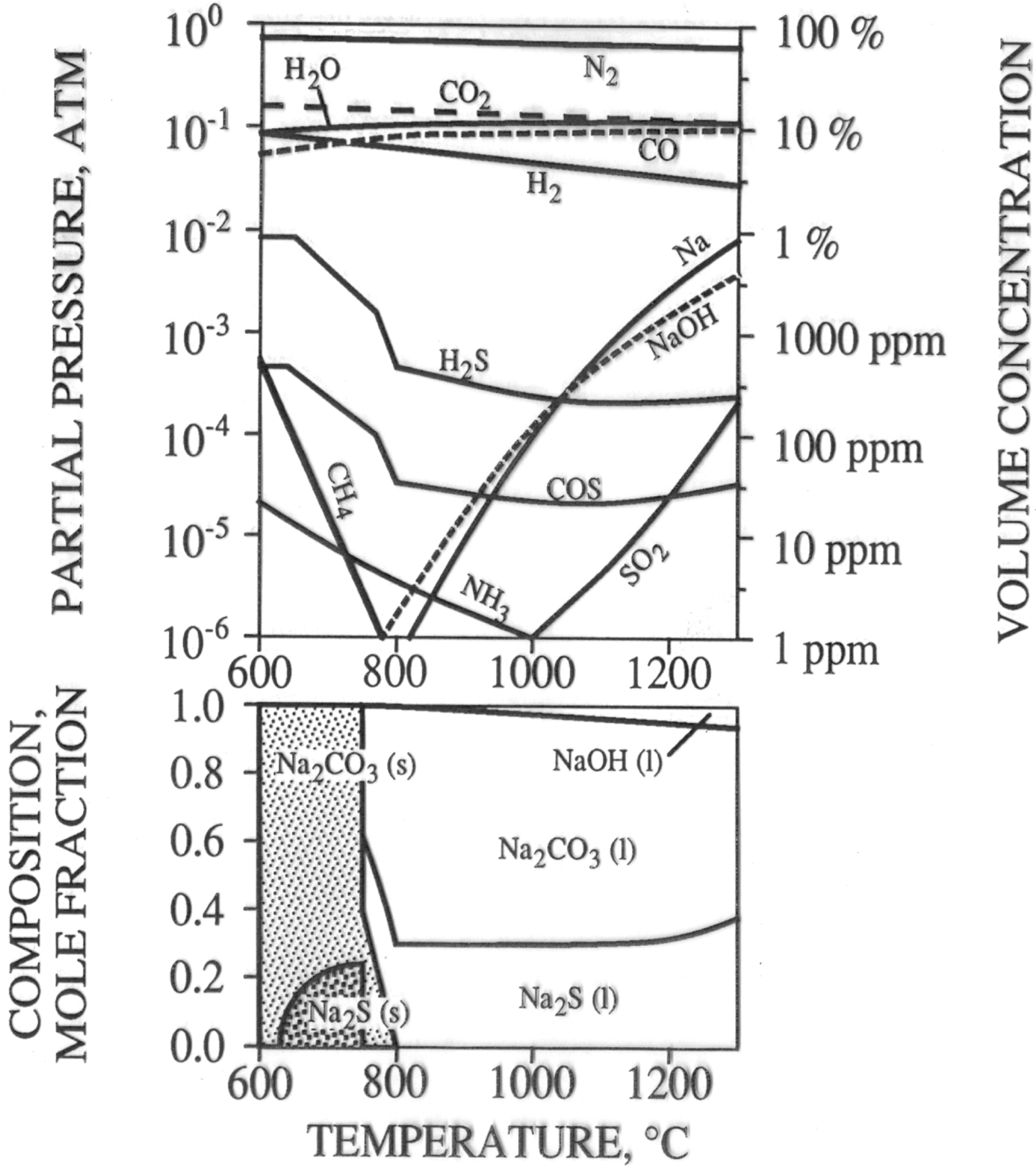
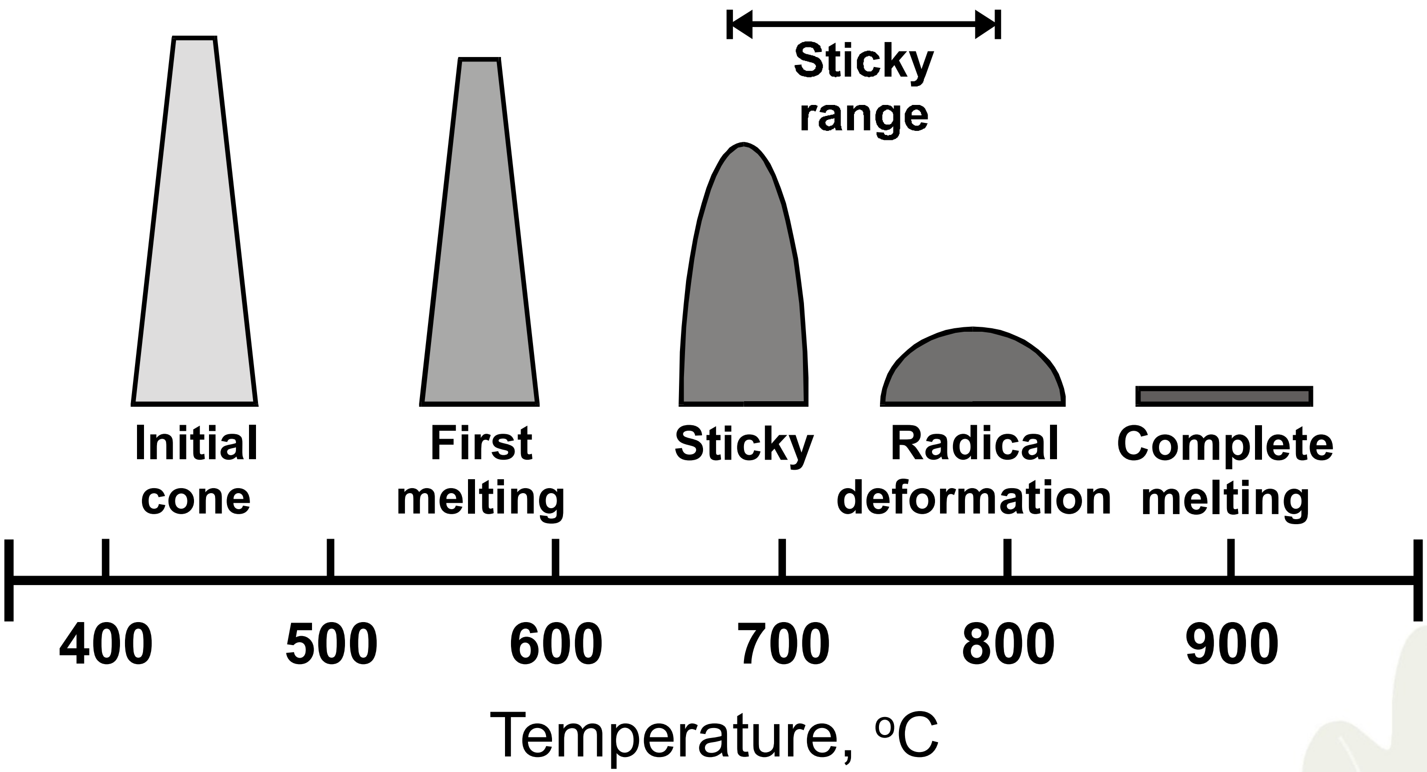


L. Pejryd, M. Hupa

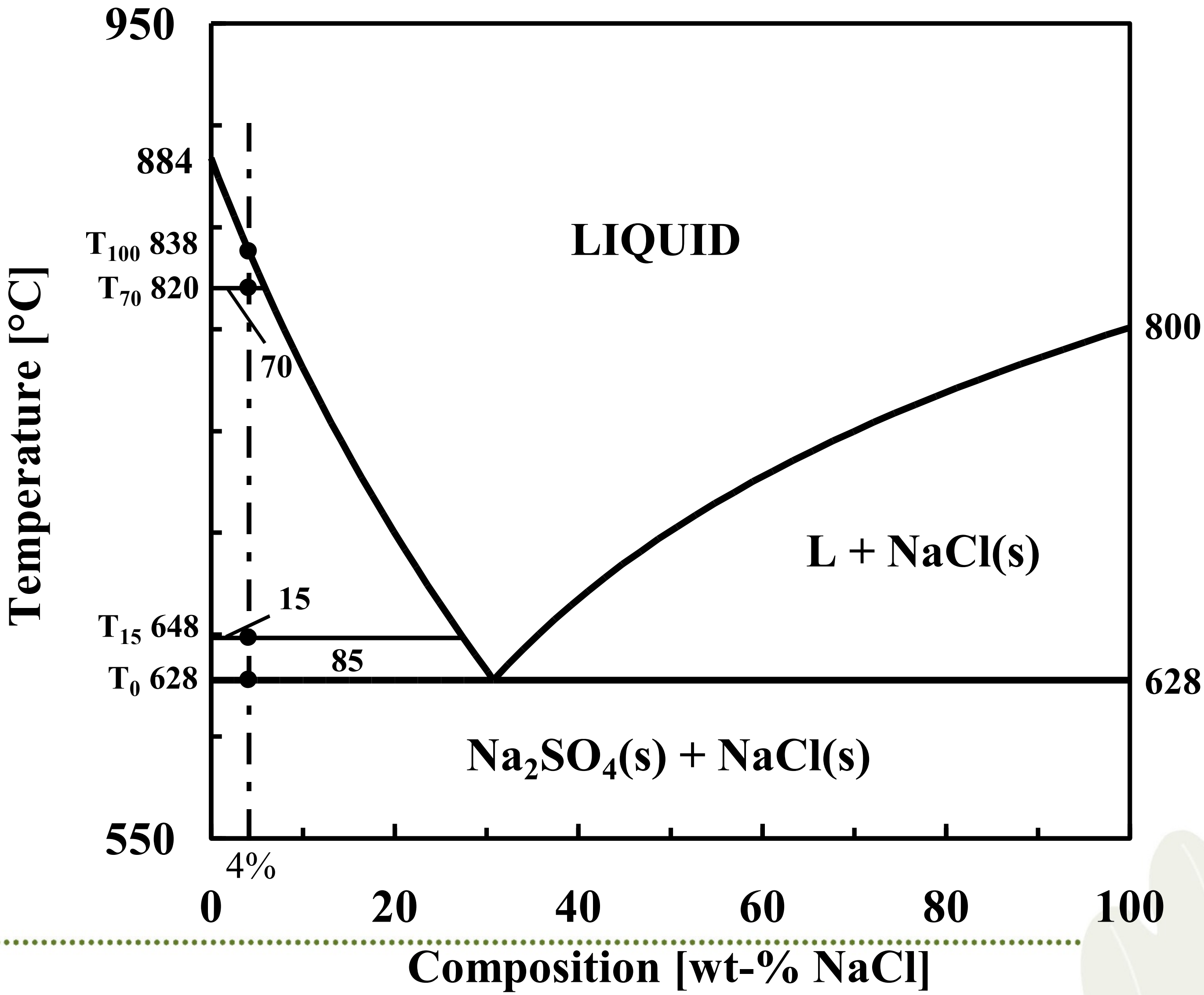
Salt Mixture Melting at Increasing Temperatures



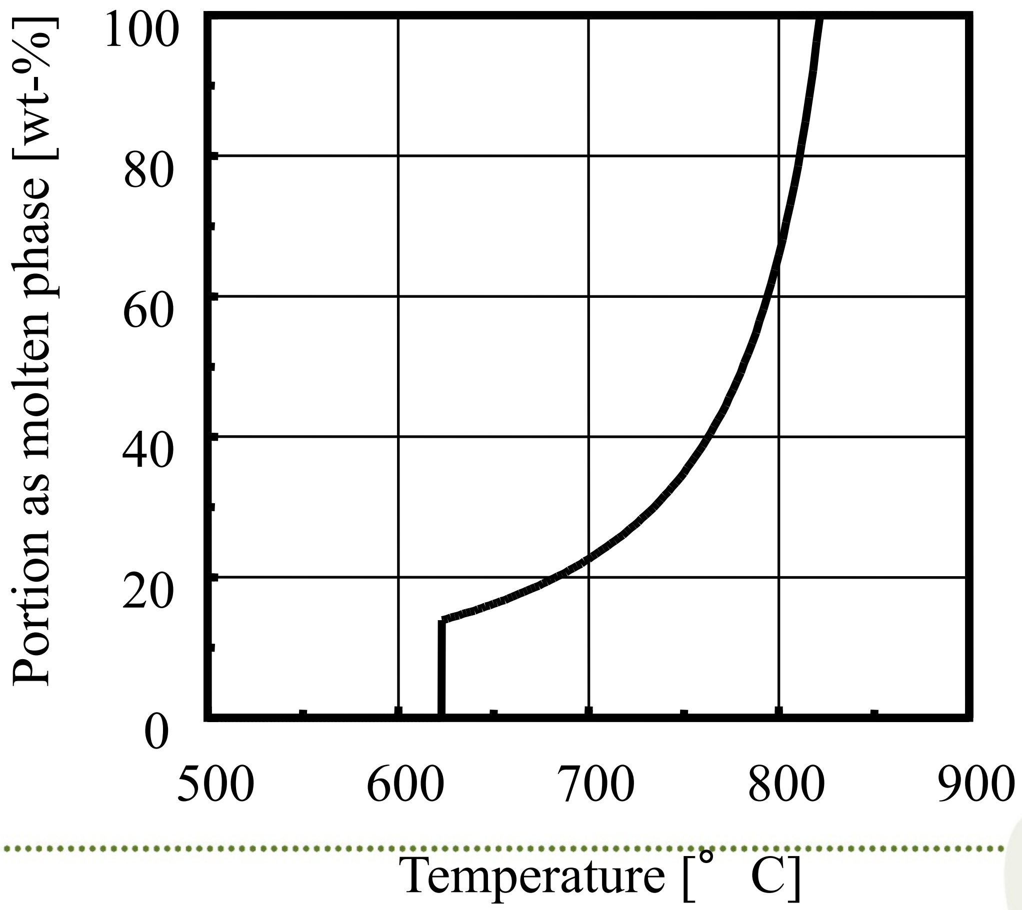
Equilibria with a Molten Phases:

Percentage of Liquid Phase

NaCl – Na_2SO_4 -system



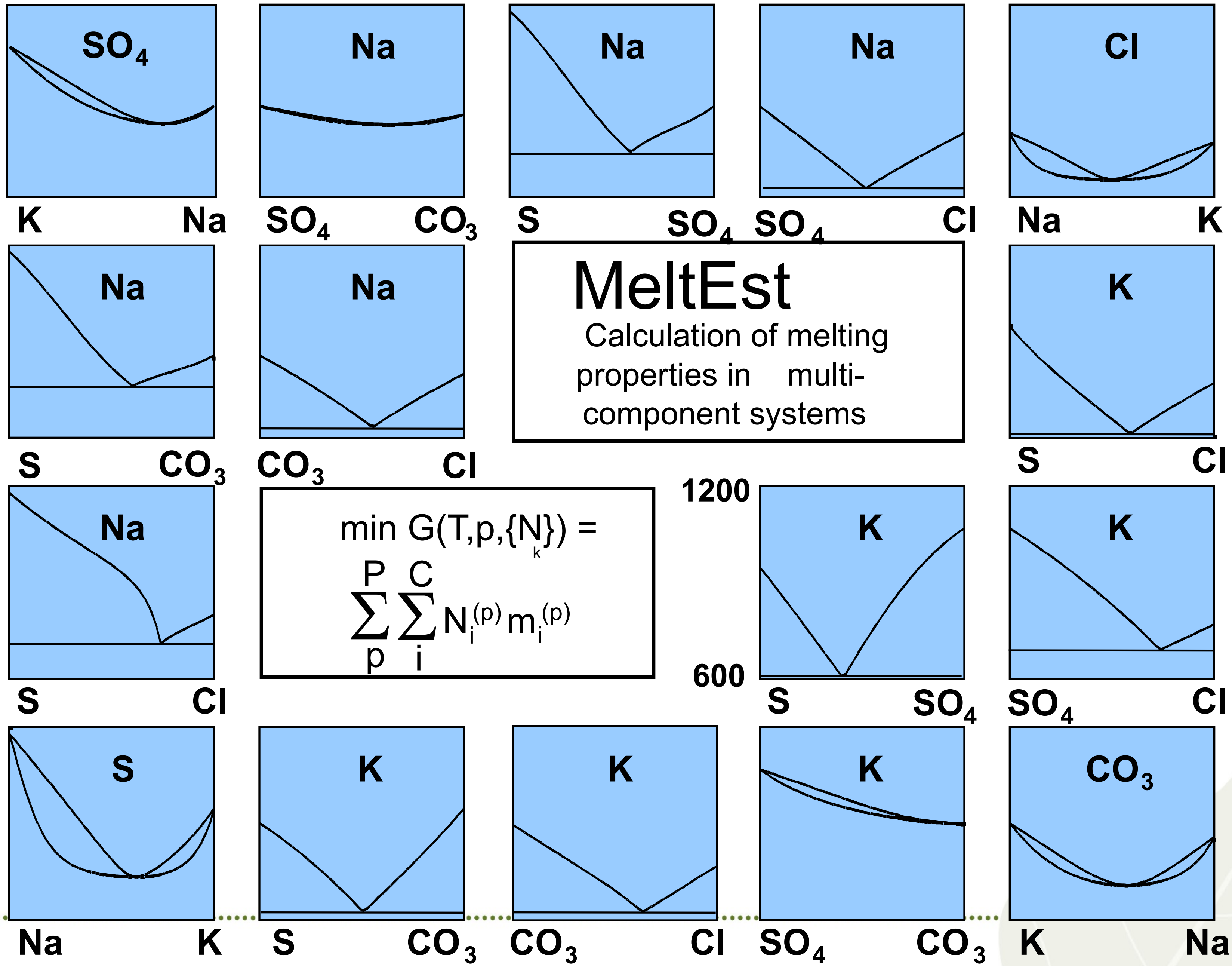
Percentage of Melt vs Temperature 4 % NaCl - 96 %NaSO4



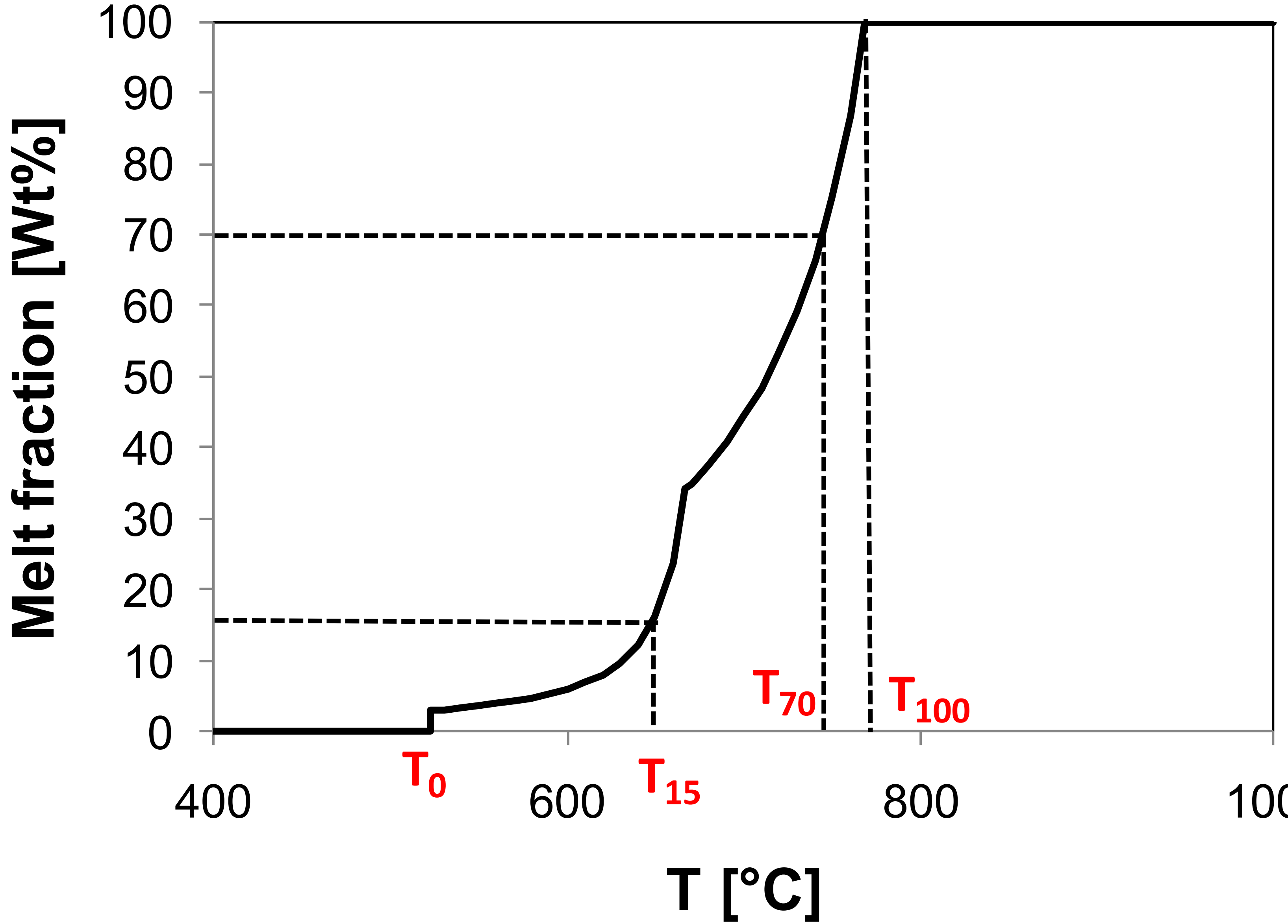
MeltEst

Calculation of melting properties in multi-component systems

$$\min G(T,p,\{N_k\}) = \sum_{p}^{P}\sum_{i}^{C} N_i^{(p)} m_i^{(p)}$$



Percentage Melt vs. Temperature for an Alkali Salt Mixture



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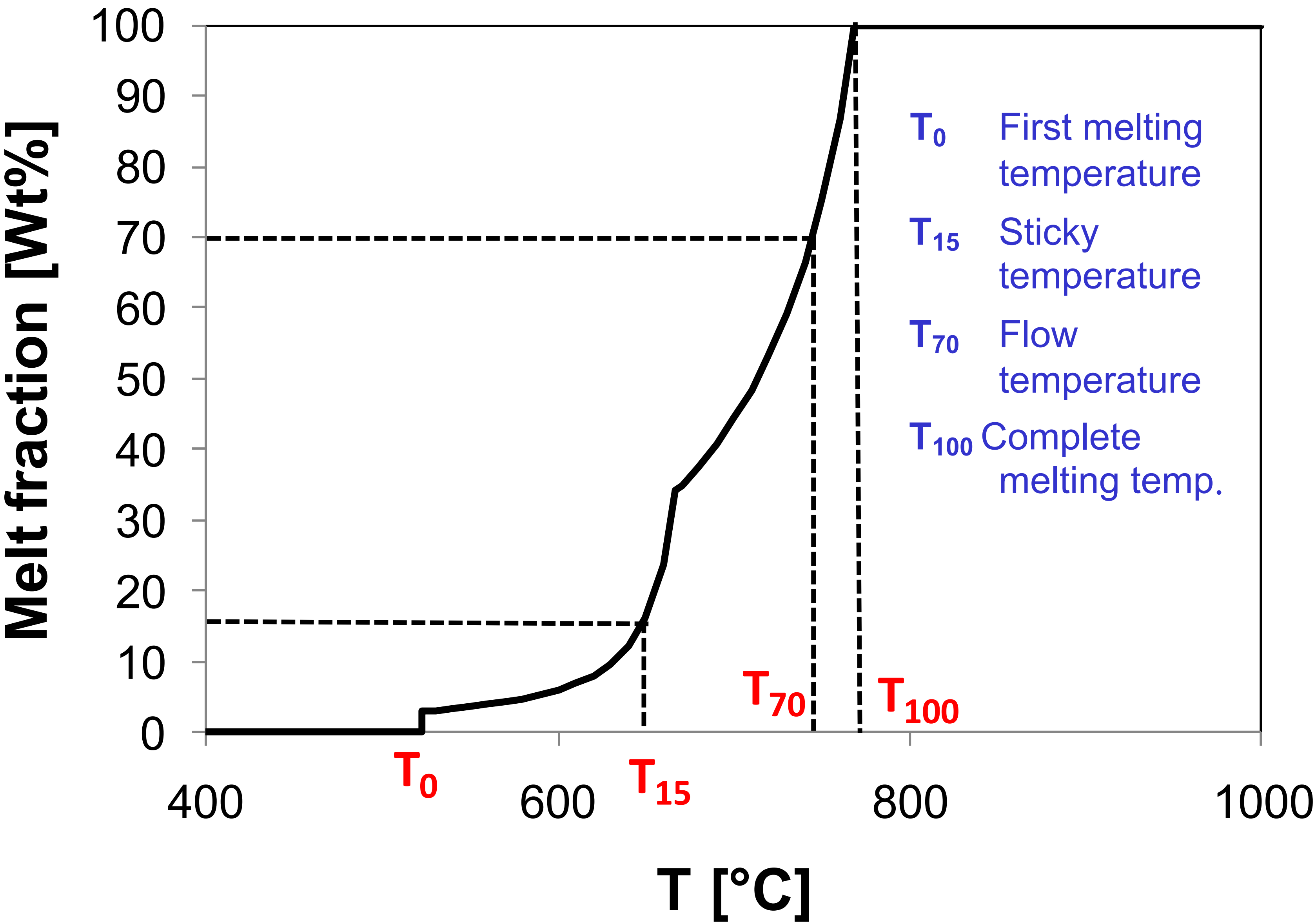
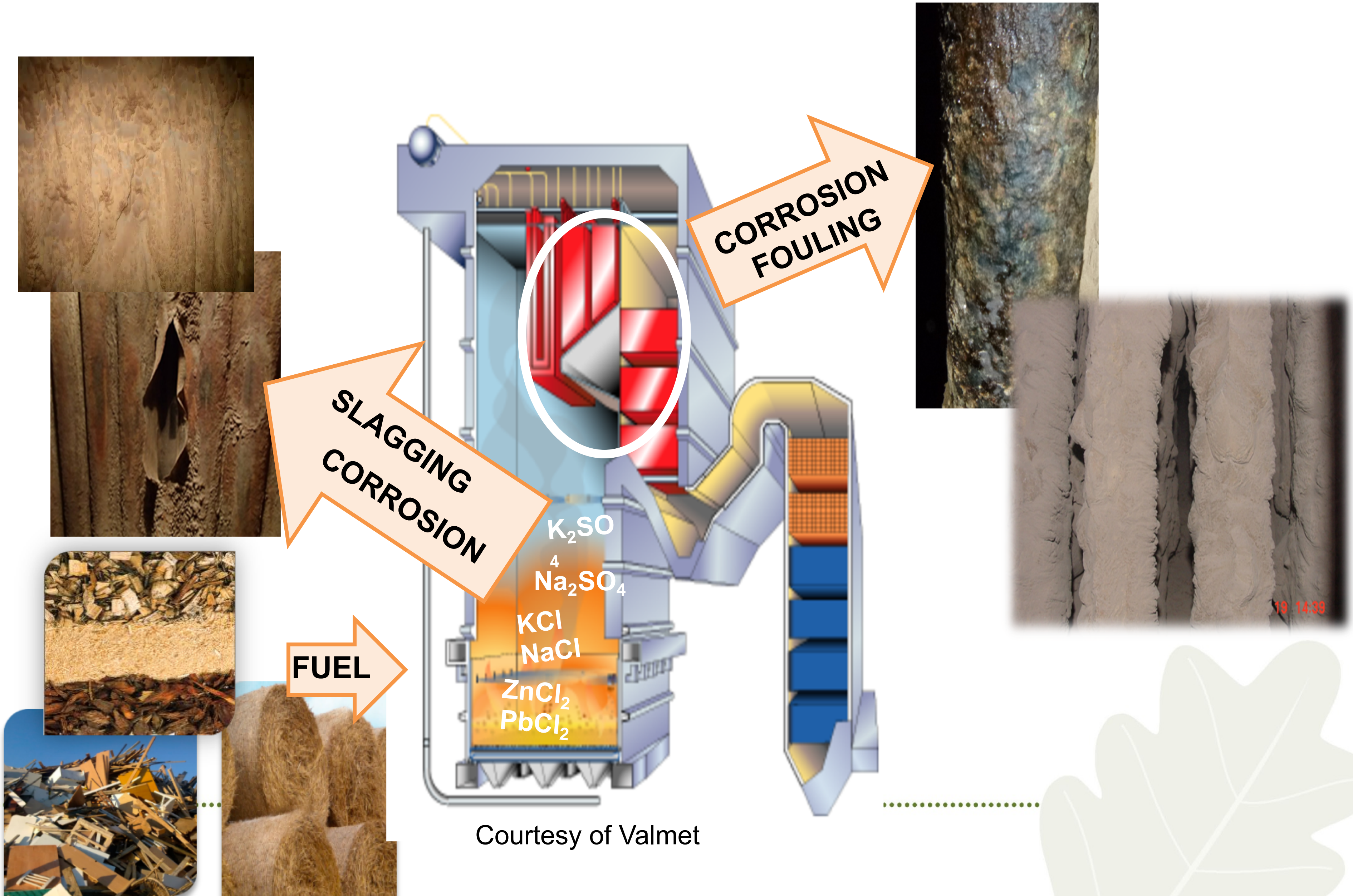


FB-combustion, ash related challenges

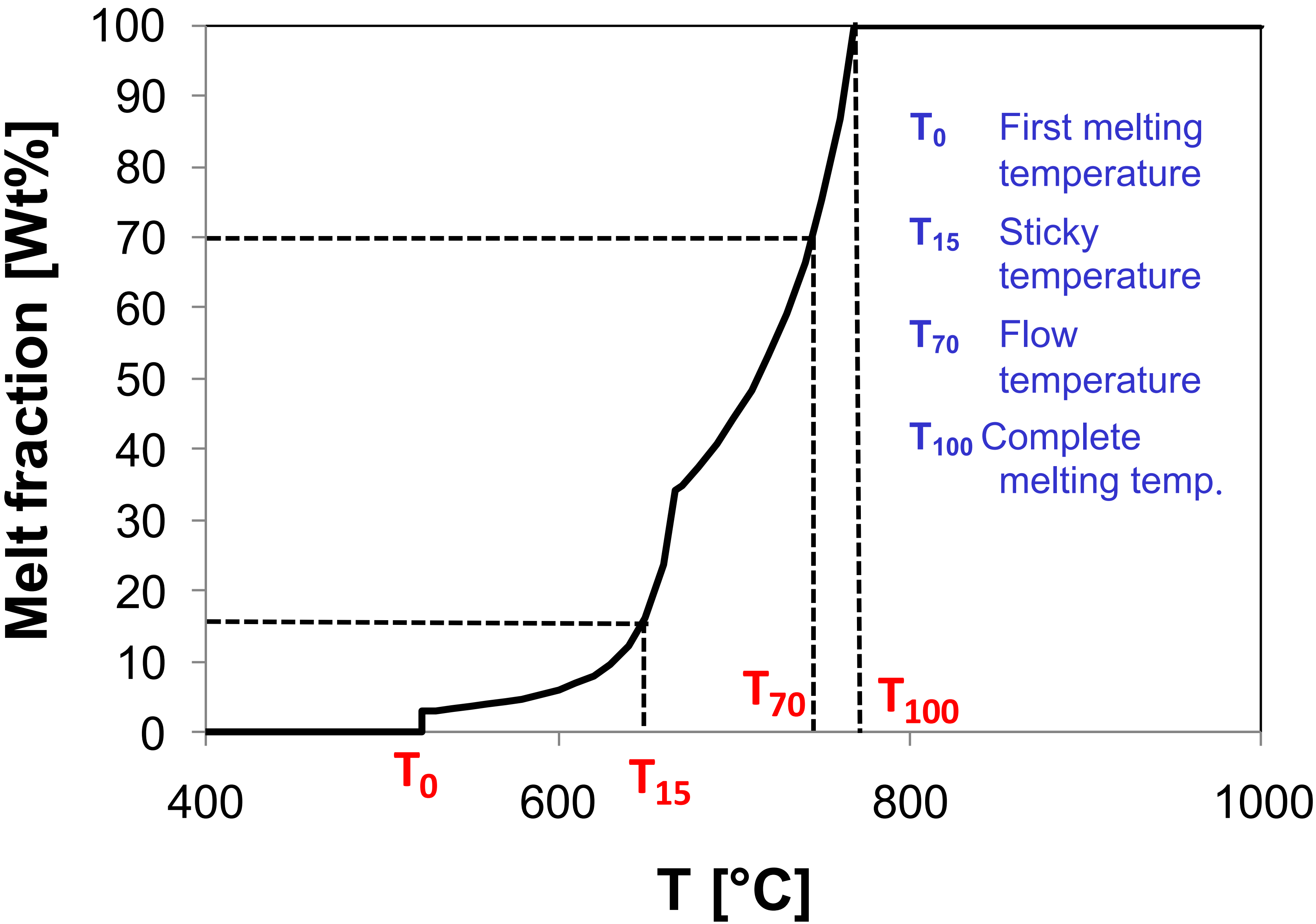


Courtesy of Valmet

Equilibria with a Molten Phases:

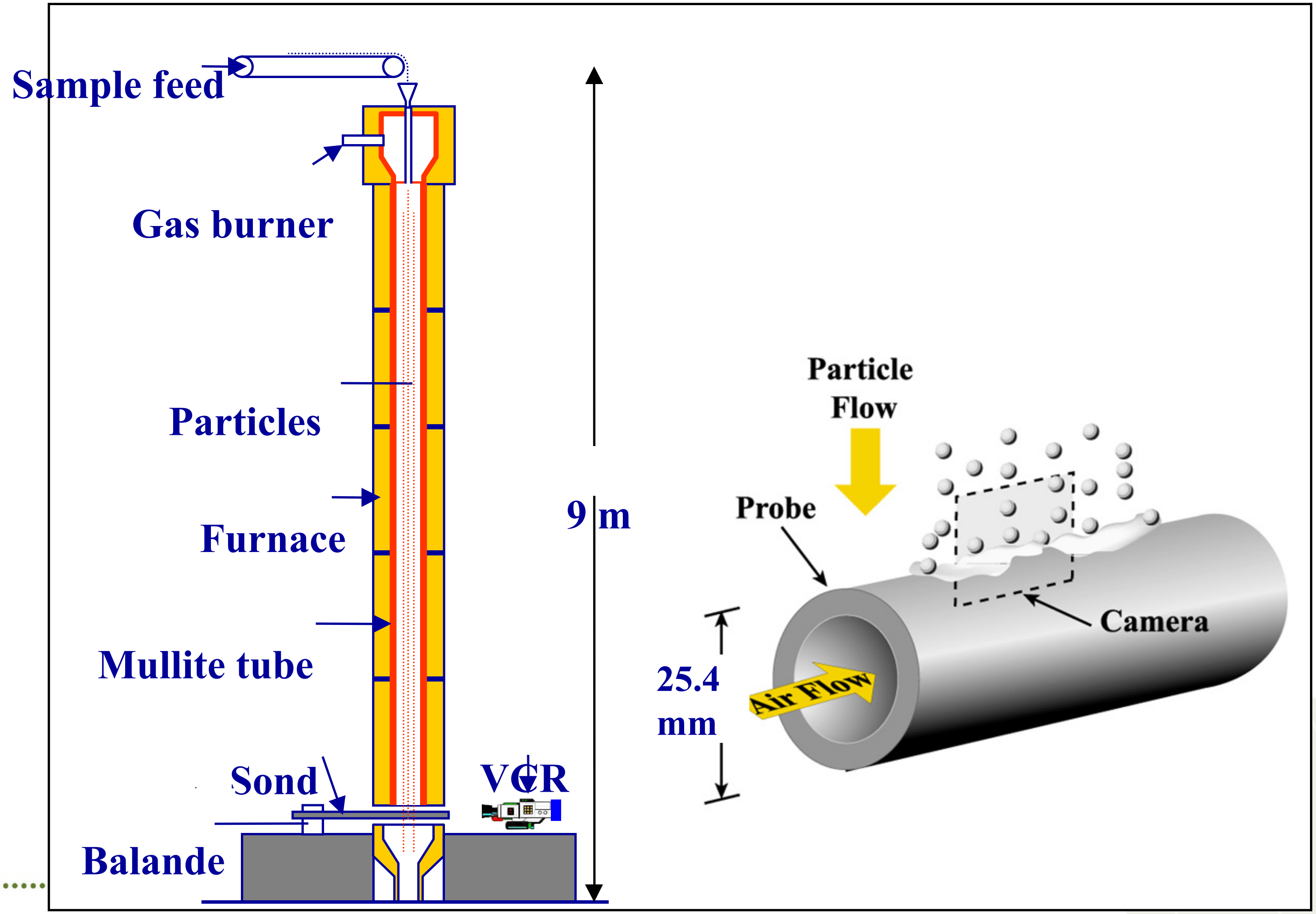
Sticky Fly Ash and T_0

Percentage Melt vs. Temperature for an Alkali Salt Mixture

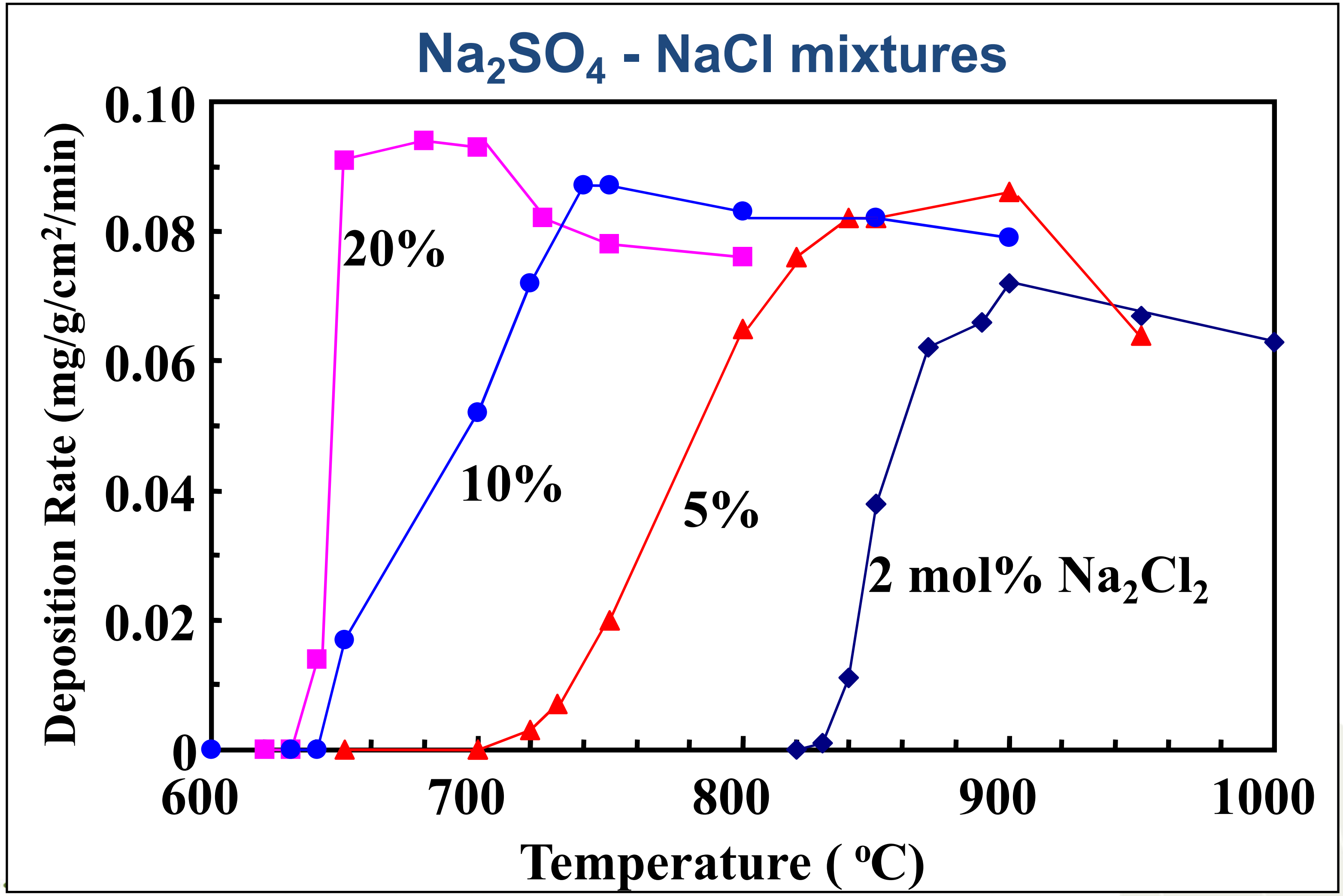


Entrained Flow Particle Reactor

University of Toronto

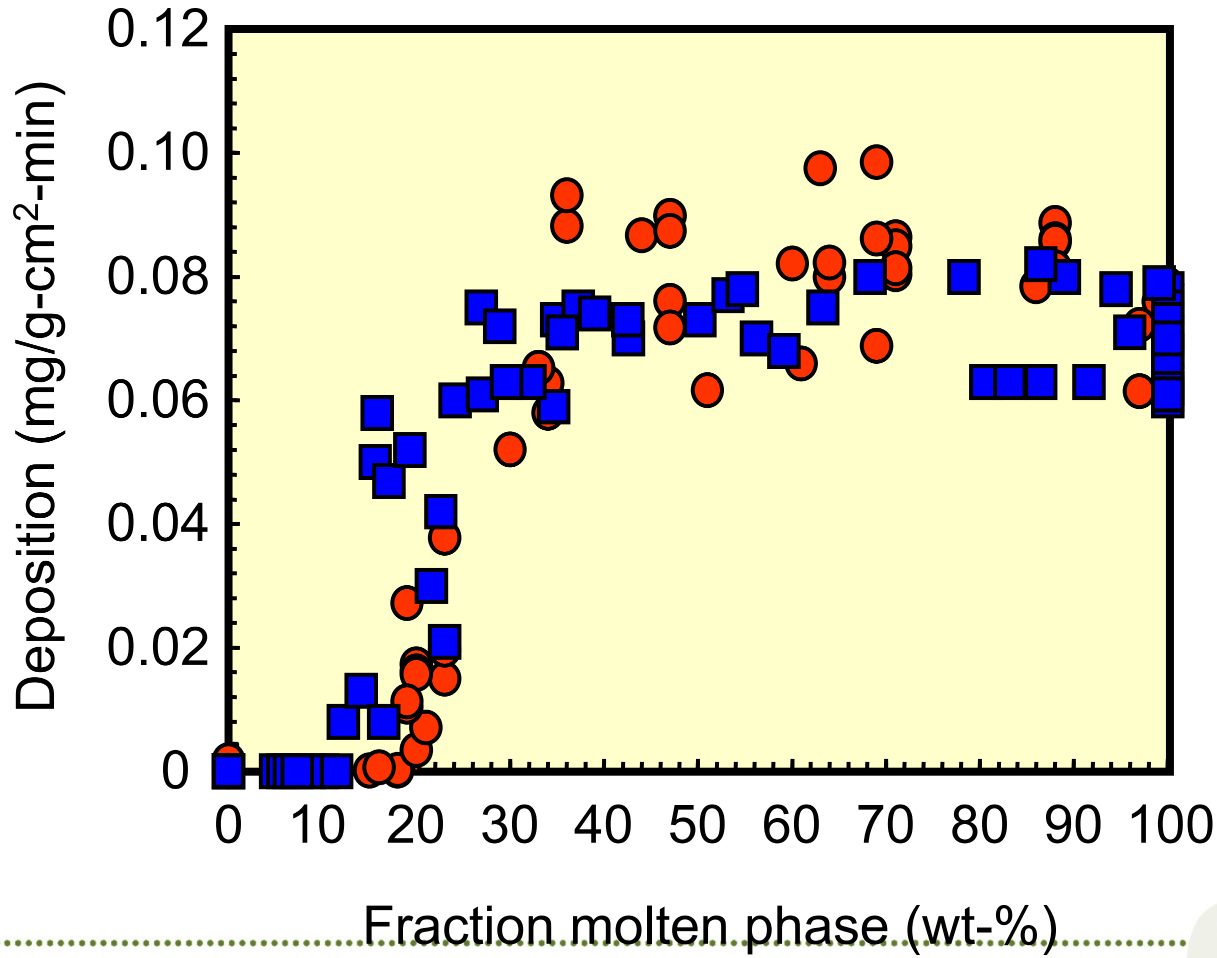


Stickiness of Salt Particles vs. Temperature and Composition



Stickiness of Partially Molten Particles

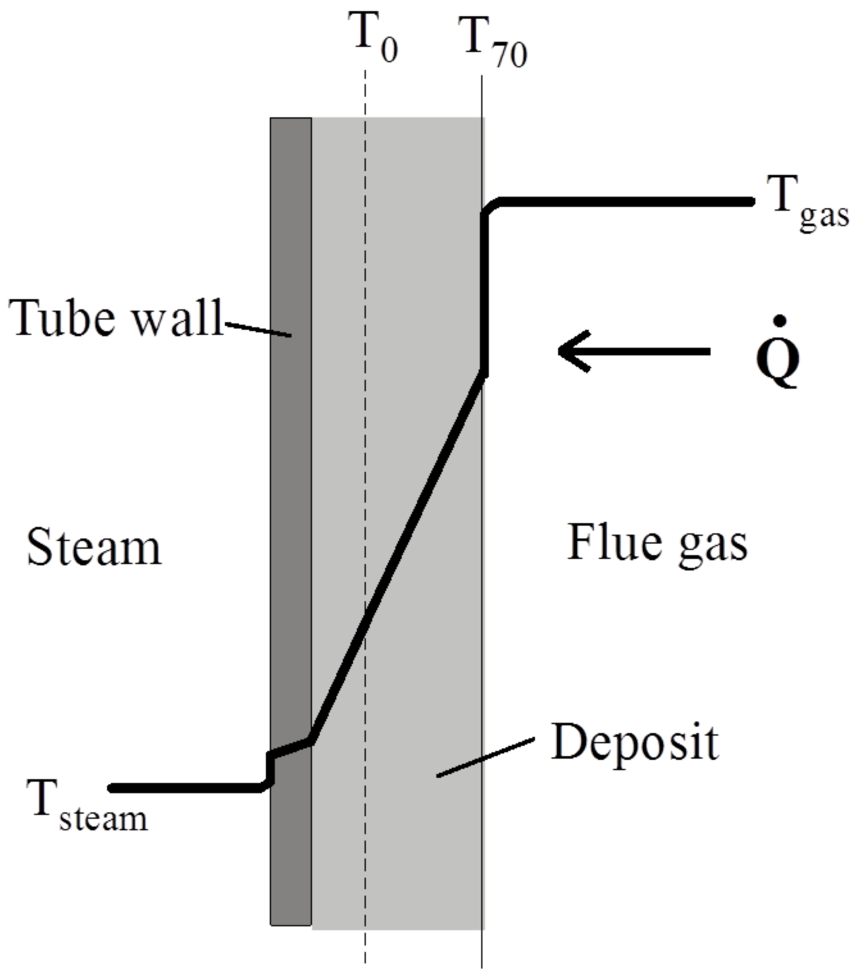
Entrained Flow Reactor Tests in Toronto



Equilibria with a Molten Phases:

Flowing Deposits and T_{70}

STEADY-STATE DEPOSIT THICKNESS



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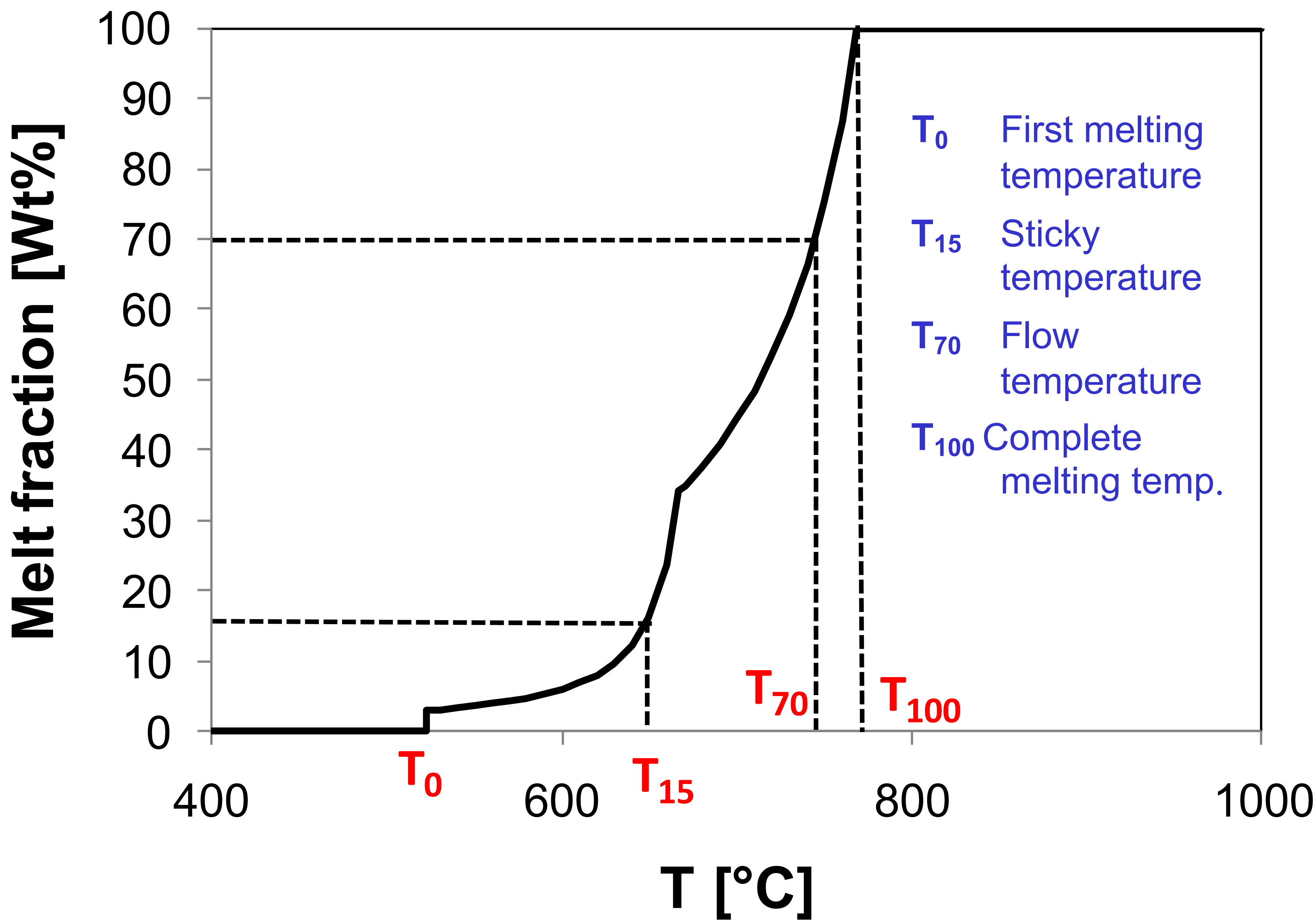


Air Cooled Probes after Exposure in Flue Gases

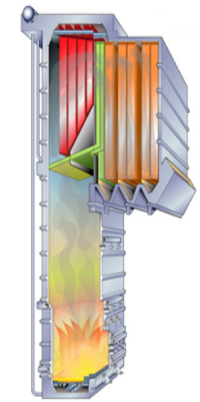
Probe Surface Temp 500 C
Flue Gas Temp 950 C

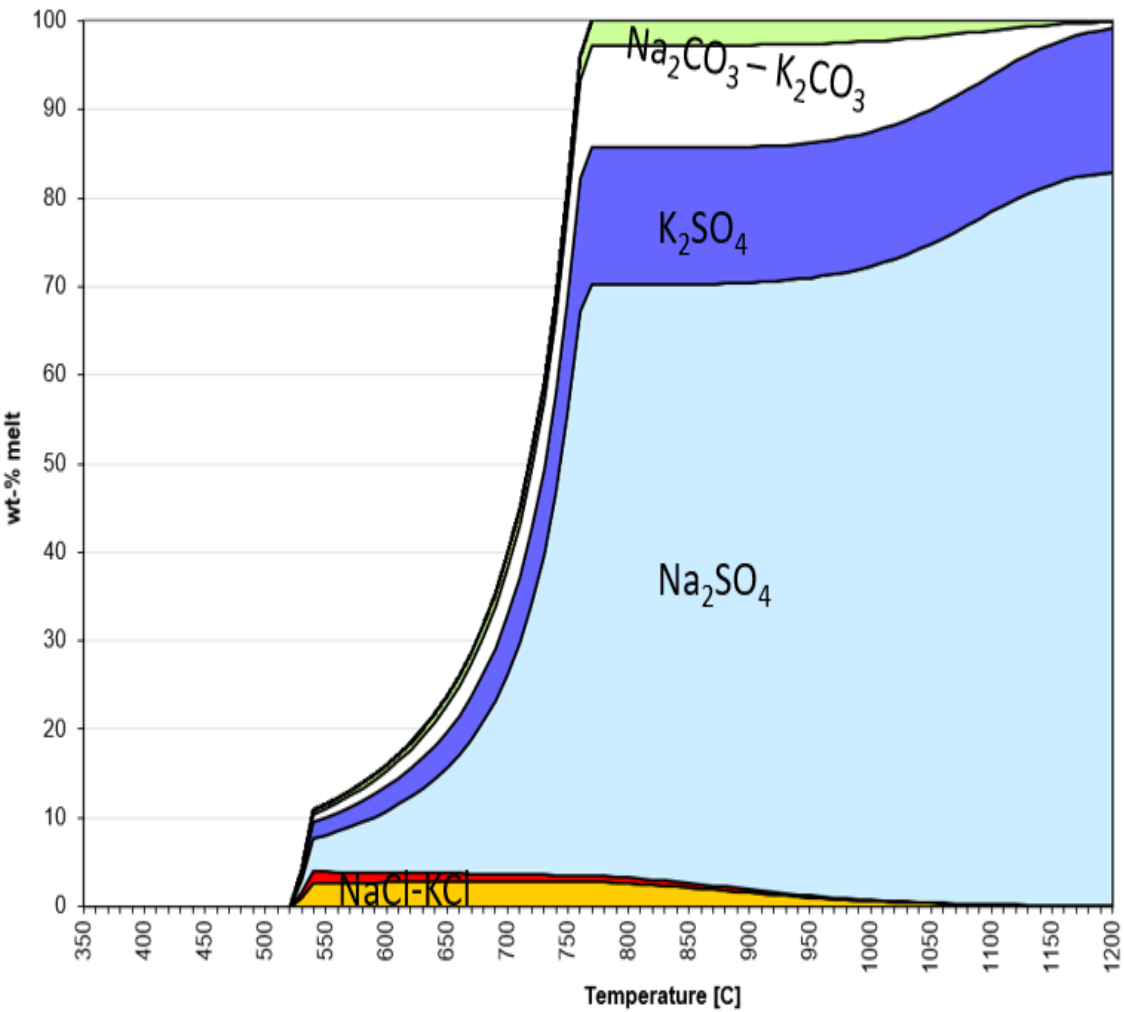
180 min

90 min

15 min

Melting temperature of ash





- $T_0 = 525$ ° C
- Sticky area:

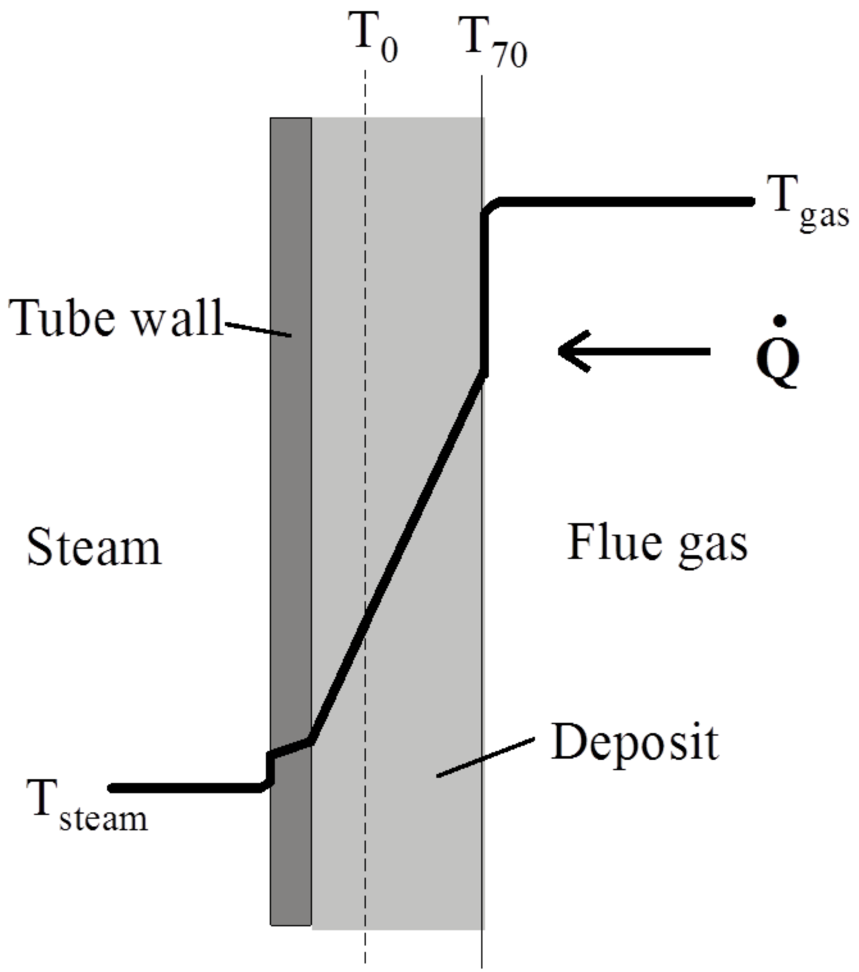
  T_{15}- T_{70} = 600-720 ° C
- $T_{100} = 750$ ° C

Hanna Kinnunen, Valmet

Equilibria with a Molten Phases:

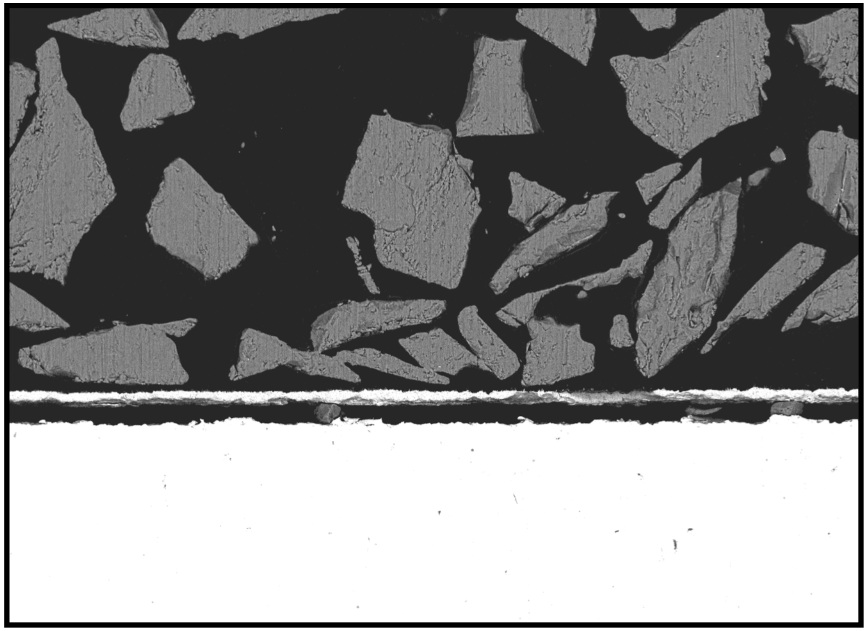
High Temperature Corrosion and T_0

STEADY-STATE DEPOSIT THICKNESS

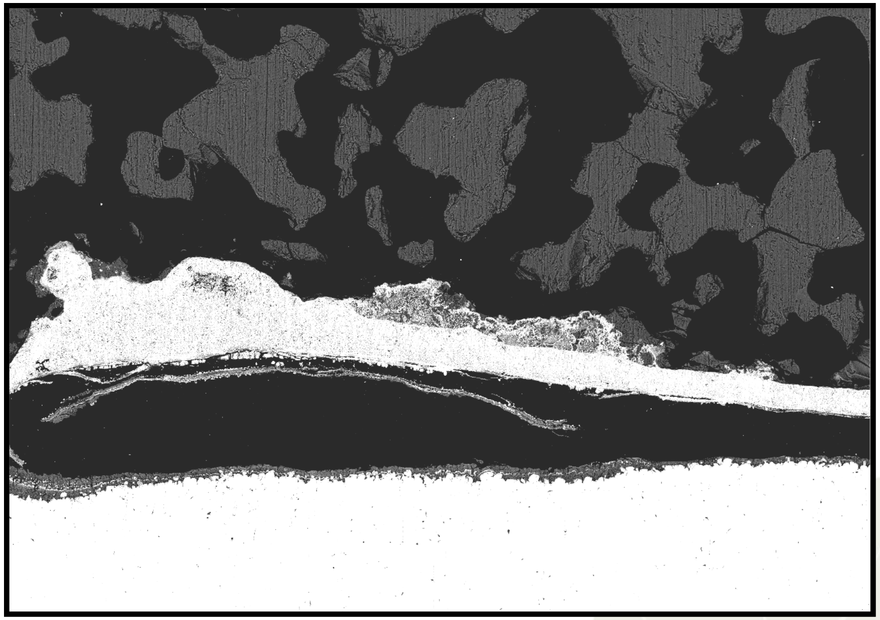


Corrosion test with alkali salt deposits on steel at 550 C

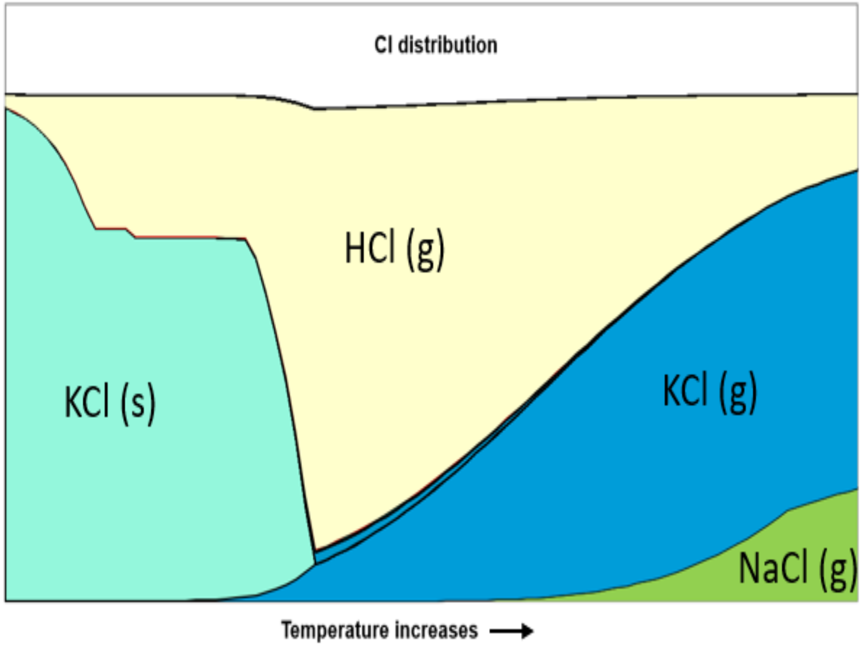
0 % molten phase in deposit



5 % molten phase in deposit



Corrosivity of a fuel mixture from thermodynamic calculations



Hanna Kinnunen, Valmet

- formation of gaseous HCl, KCl and NaCl
- condensation of solid KCl

→ corrosion risk in superheater area

- correlating results to empirical corrosion data from existing boilers

→ superheater material selection and corrosion rate estimation

Equilibrium Calculations in Combustion Systems

- Gaseous Combustion Equilibria
- Solid-Gas Equilibria
- Equilibria with a Molten Phase
- **Equilibria and NOx**

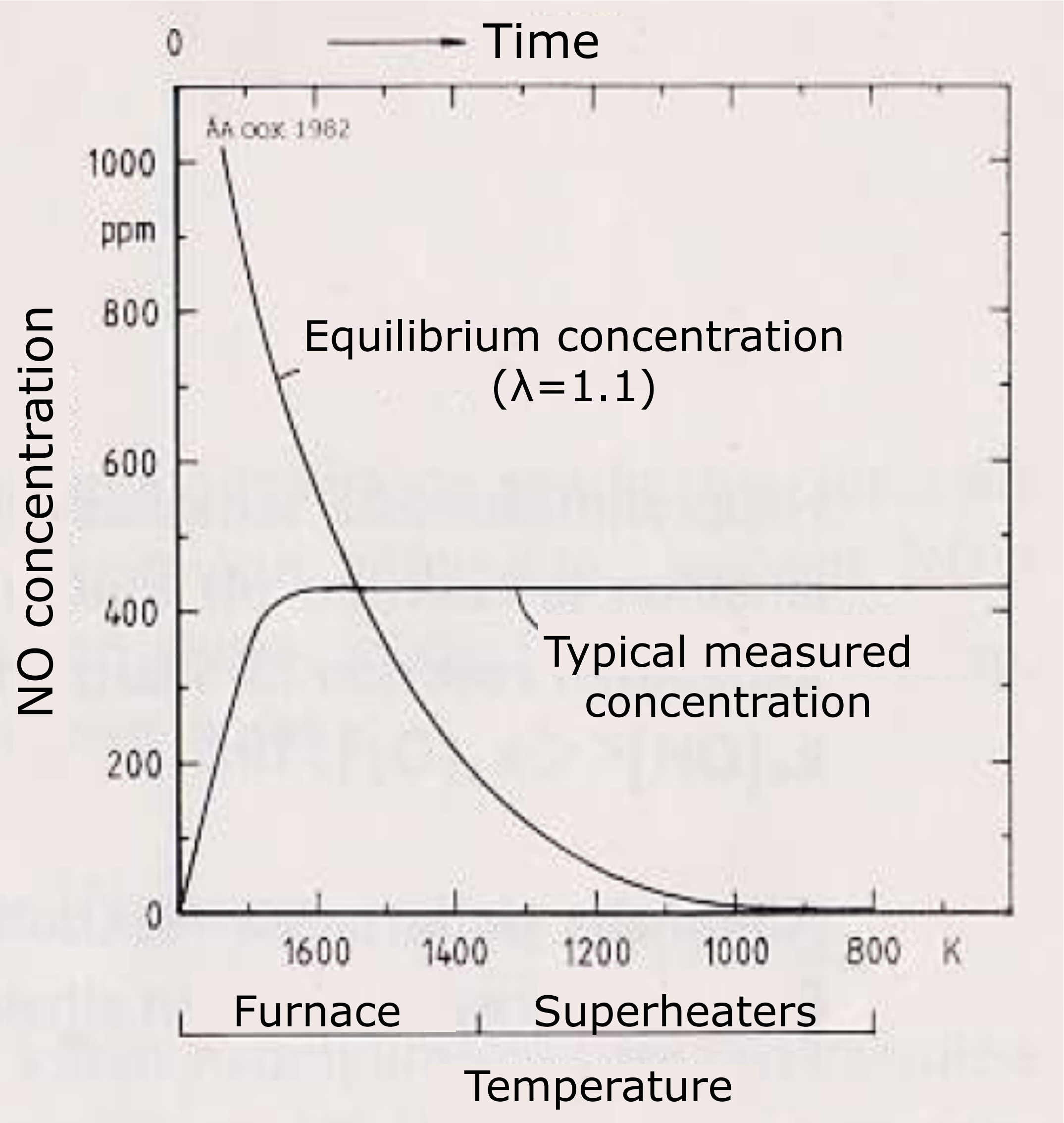
Nitrogen species in a typical flue gas under chemical equilibrium conditions

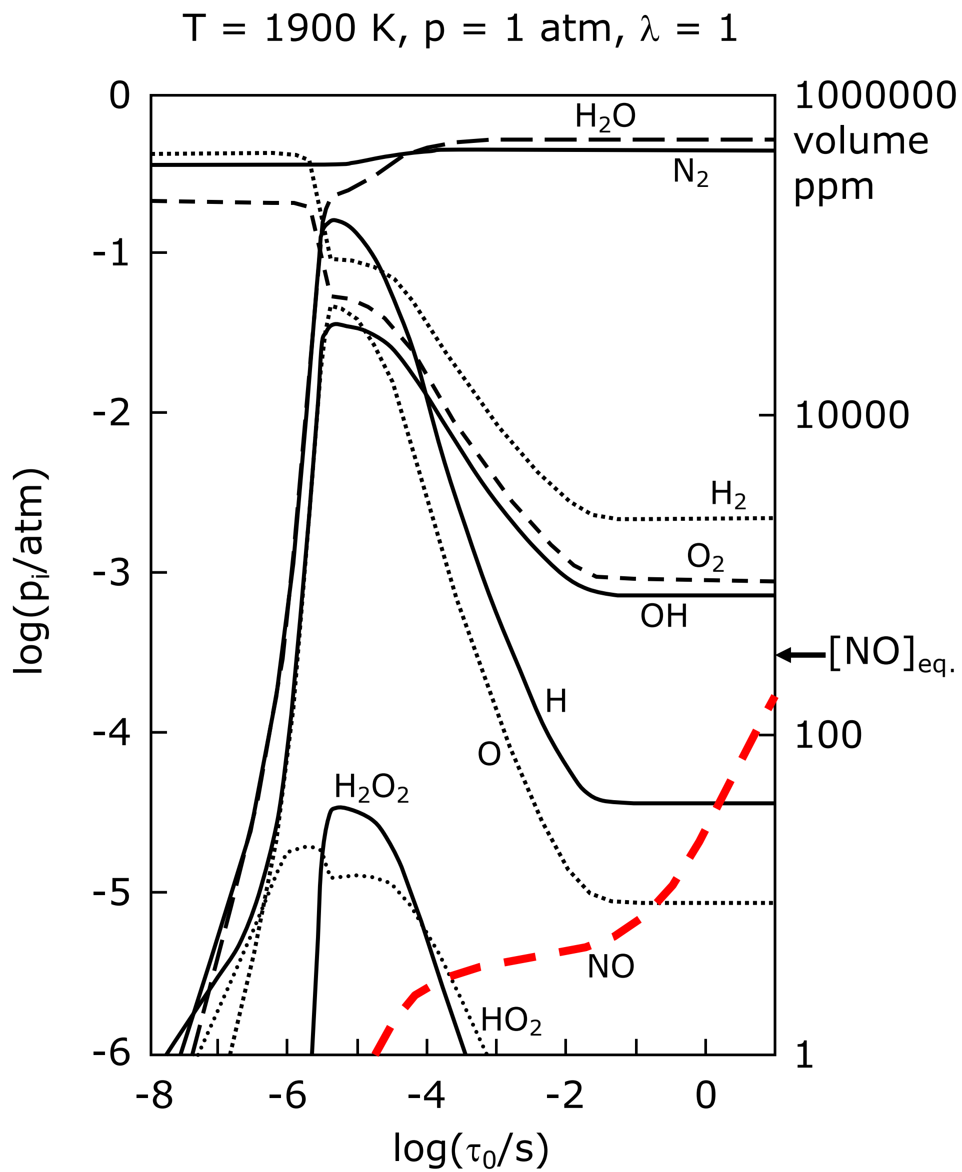
- Most abundant ones
  λ=1.1: N_2, NO, NO_2, N_2O
  λ=0.9: N_2,HCN, NH_3

- Equilibrium conc. of NO_x decreases with temp.
  data from flue gas with λ=1.1:

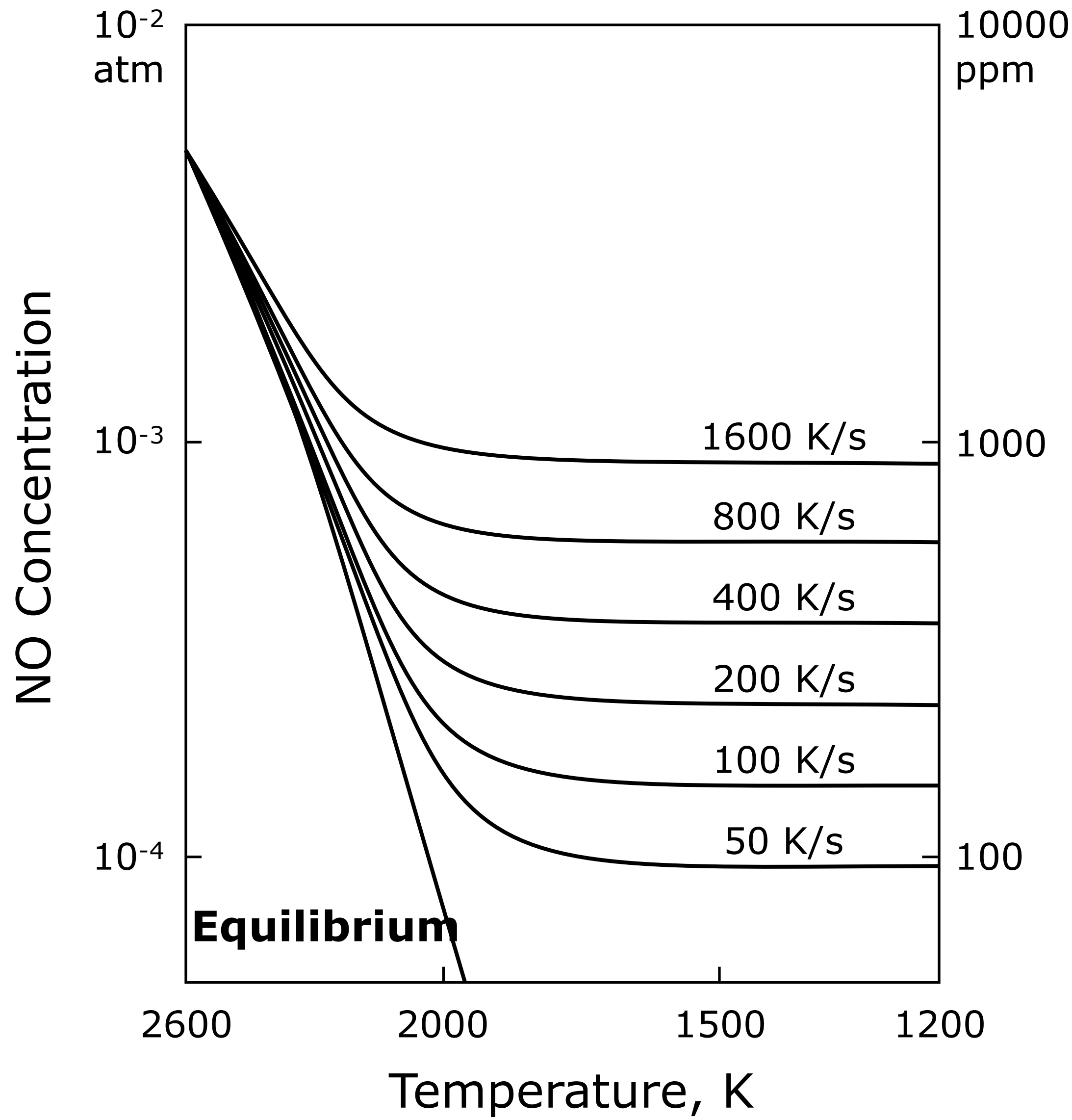
T=1800 K	1200 ppm
T=500 K	<1ppm

Schematic view of NO Formation in Boilers
- Chemical Equilibrium vs. Kinetics



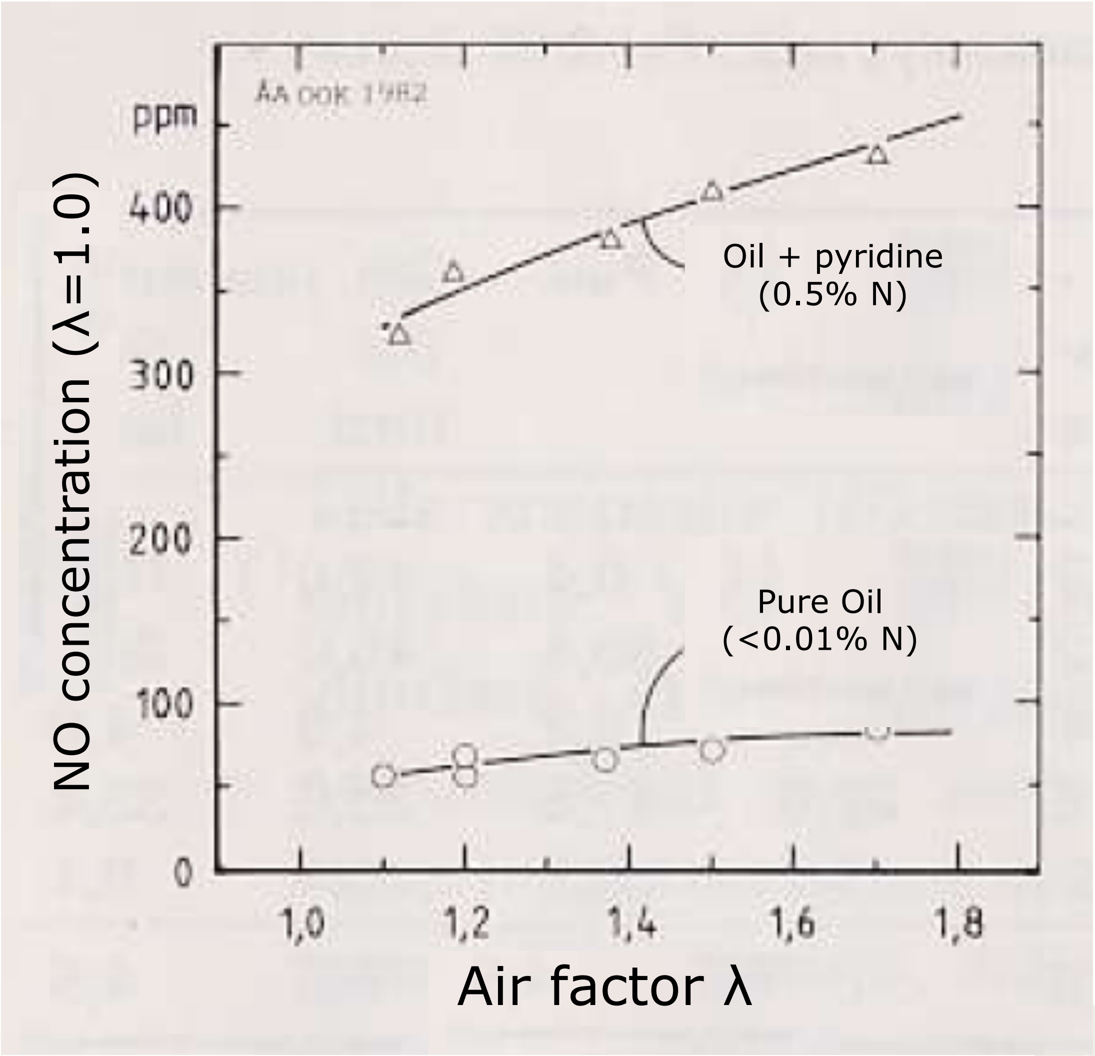


Combustion of Natural Gas with Air.
Kinetic Modeling.



NO concentration in cooling flue gases. Curves for different cooling rates. (Methane/air flue gas at $\lambda = 0.9$)

NOx – Fuel Oil with Organic Nitrogen Addition



Based on Martin and Berkan, Air pollution and its control, AICHE symp. Series 68, Nr 126, 45, 1972

Equilibrium and NOx

- Forget - except at very high temperatures (2500+ ° C)
- Formation chemistry slow and sensitive to initial form of input nitrogen (N_2, org-N)
- Decomposition chemistry ”frozen” at below 1500 ° C

Equilibrium Modelling (EM) and Combustion - Conclusions

- Gas phase: EM standard and relevant (but T > 800 ° C)
- Solid-gas: EM gives boundary conditions for gas-solid reactions
- Kinetic information needed of the extent of solid conversion
- Molten phases: EM well developed for simple alkali salts
- Percentage liquid phase interesting for melt rheology, stickiness and corrosion
- Work needed to expand the melt system
- NOx: Forget EM except > 2500 ° C!
  (Kinetic models available)

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