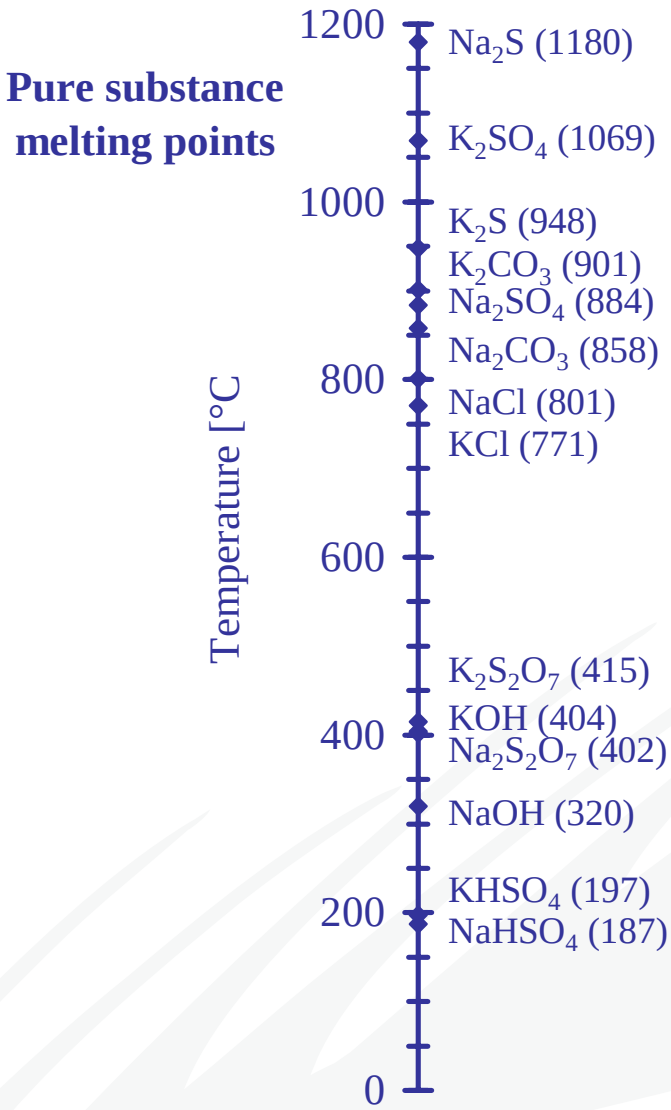
2. Melting Equilibria and Ash Behavior

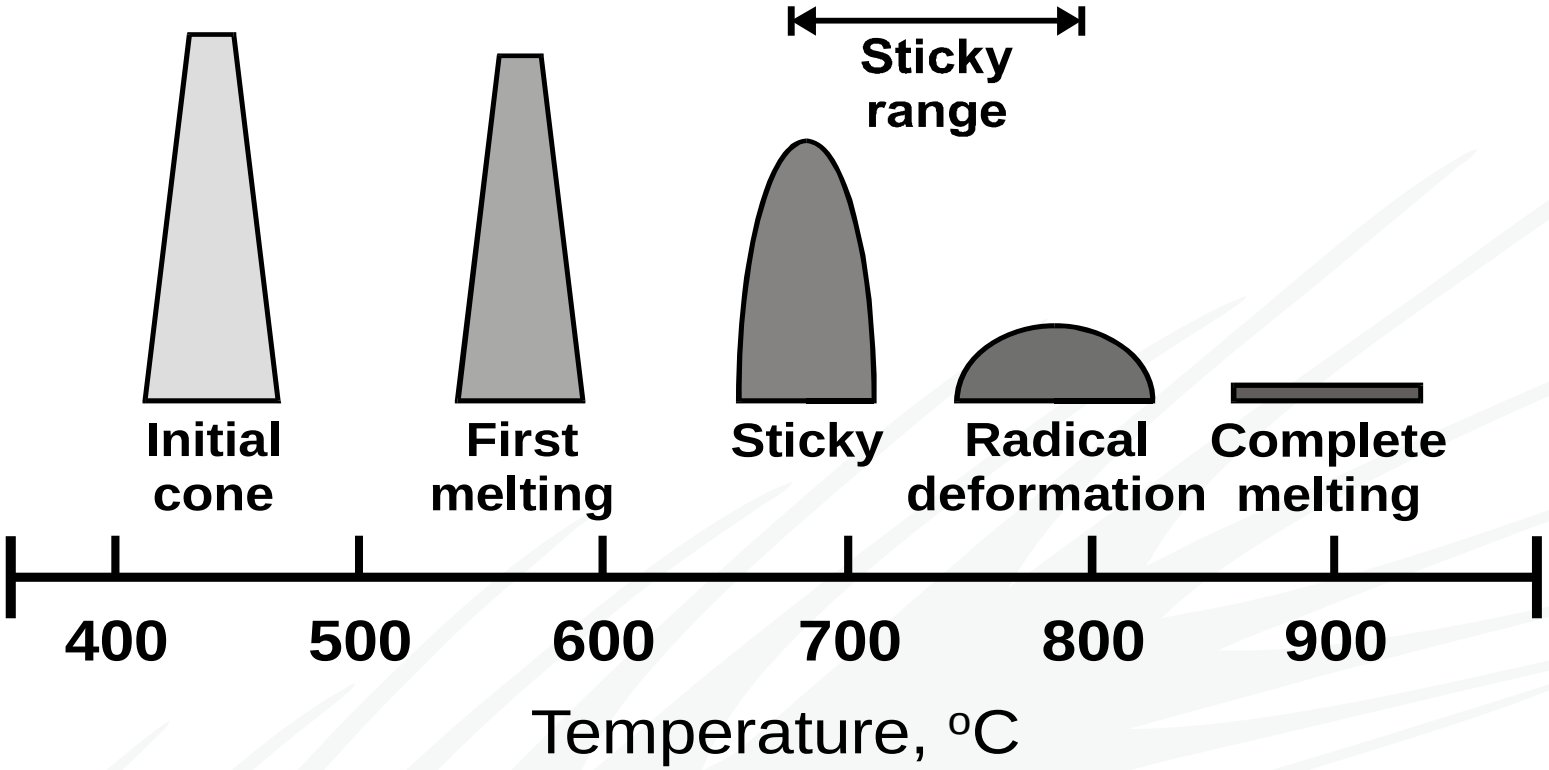
Melting Equilibria and Ash Behavior - Terms and Concepts

- Melting equilibrium
- Liquidus
- Solidus
- Eutectics
- Lever rule
- Percentage of molten phase
- Intermediate compounds
- Solid solution
- Partial solid solubility
- Thermodynamic modelling of melting
- T_{15} and stickiness
- T_{70} and flowing
- T_0 and corrosion

Melting of salts and salt mixtures


Pure substance melting points
Temperature [°C
1200
1000
800
600
400
200
0
Na2S (1180)
K2SO4 (1069)
K2S (948)
K2CO3 (901)
Na2SO4 (884)
Na2CO3 (858)
NaCl (801)
KCl (771)
K2S2O7 (415)
KOH (404)
Na2S2O7 (402)
NaOH (320)
KHSO4 (197)
NaHSO4 (187)

Salt Mixture Melting at Increasing Temperatures



Melting temperature of salts and their mixtures (50/50 mol/mol)

K_2SO_4: 1069 C – K_2CO_3: 901 C

Na_2SO_4: 881 C – NaCl: 801 C

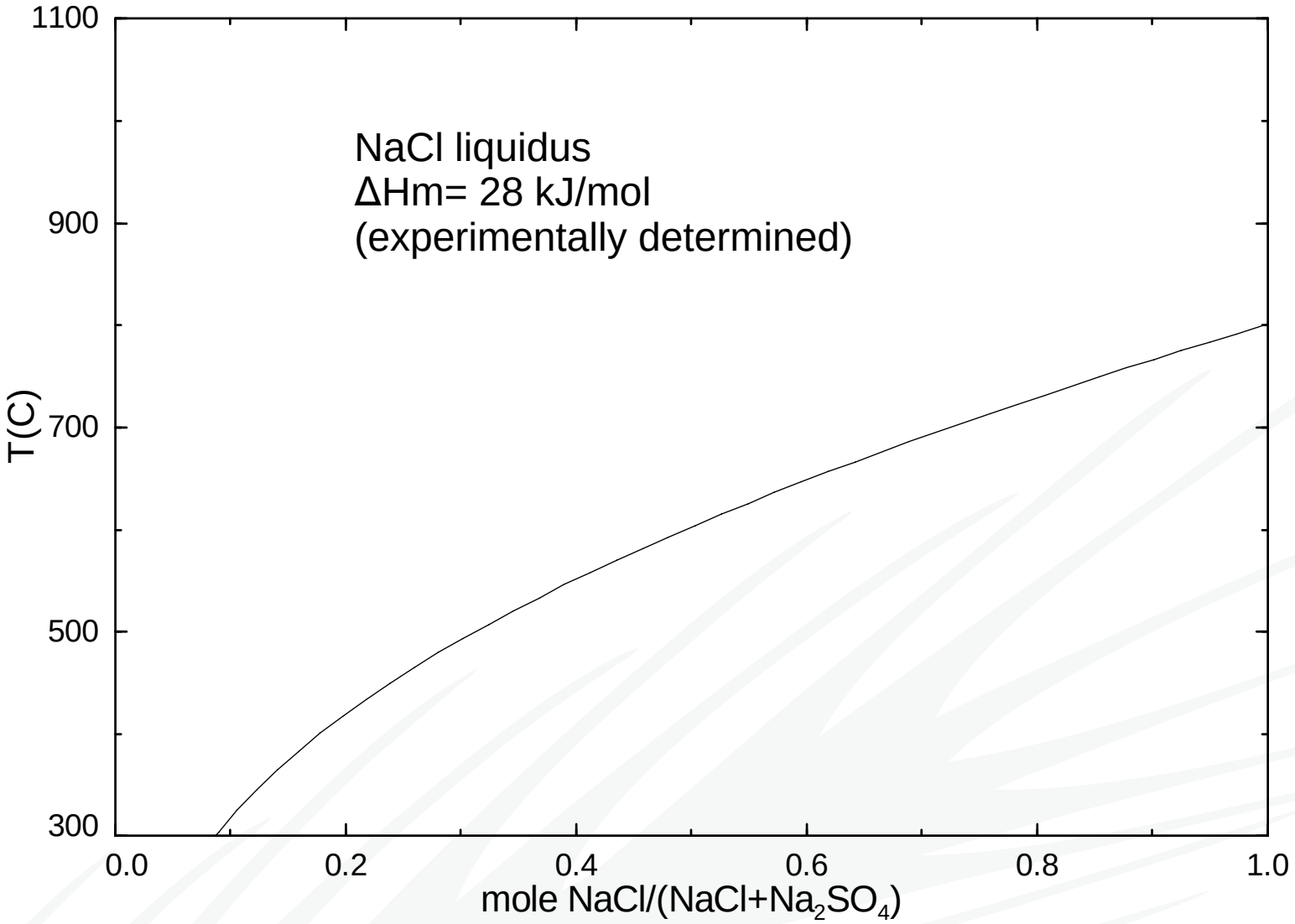
Liquidus Curve
- Freezing Point Depression

$$\ln X_{A(l)} = \Delta H_m/R\ (1/T_m - 1/T)$$

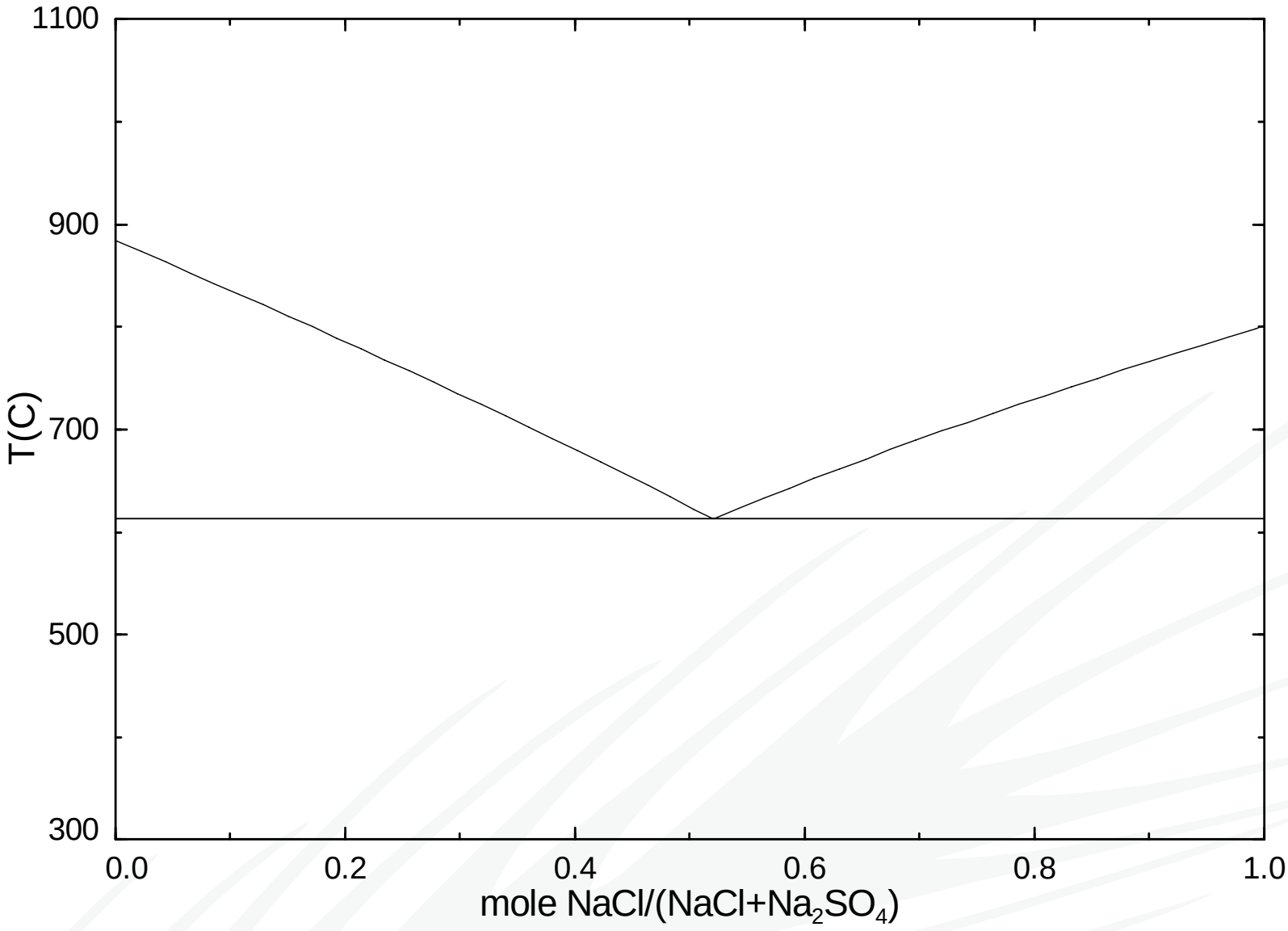
Calculation of phase diagram Na2SO4-NaCl

Na2SO4 liquidus
ΔHm= 23 kJ/mol
(experimentally reported)

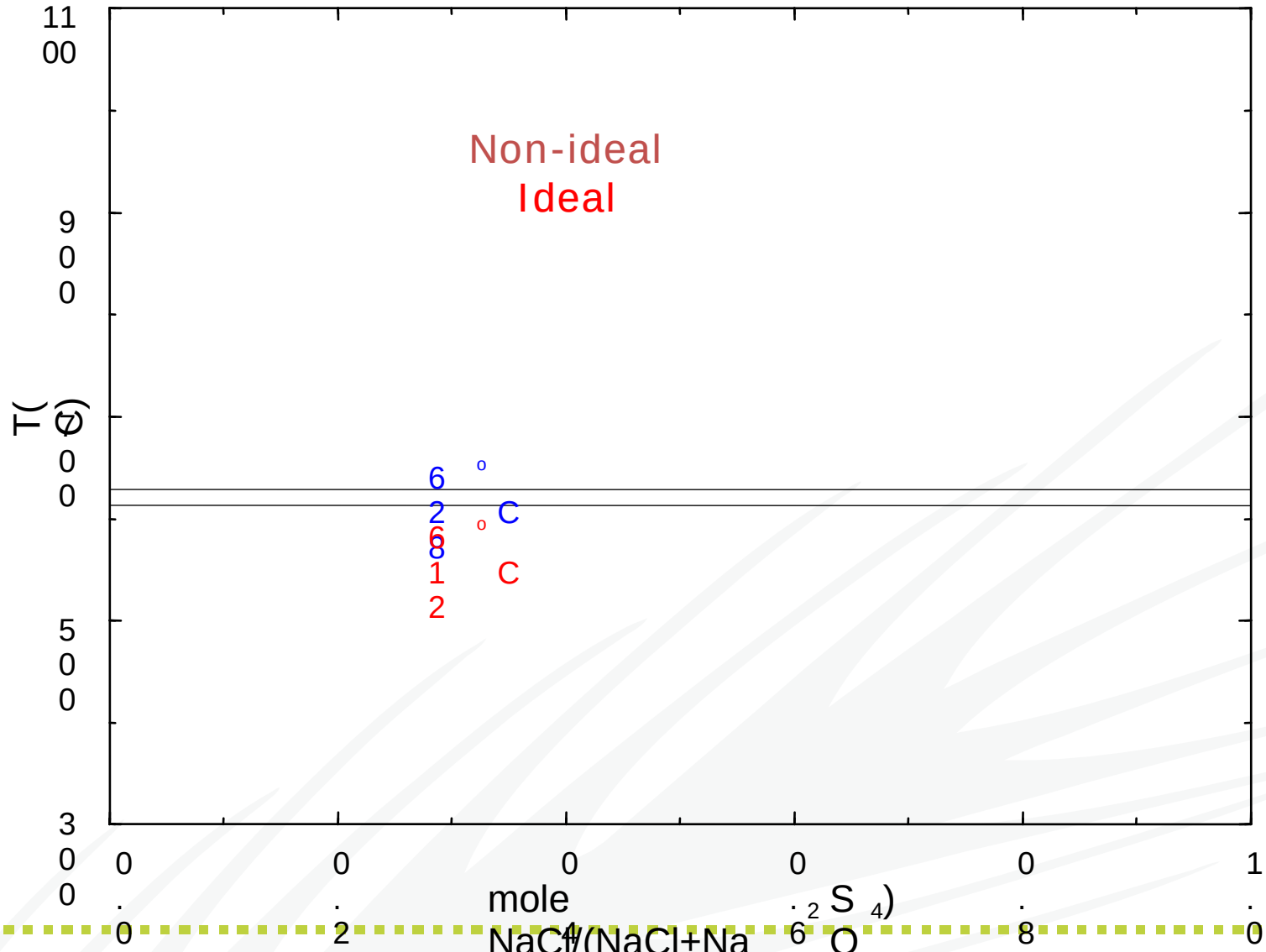
Calculation of phase diagram Na2SO4-NaCl



Phase diagram Na2SO4-NaCl



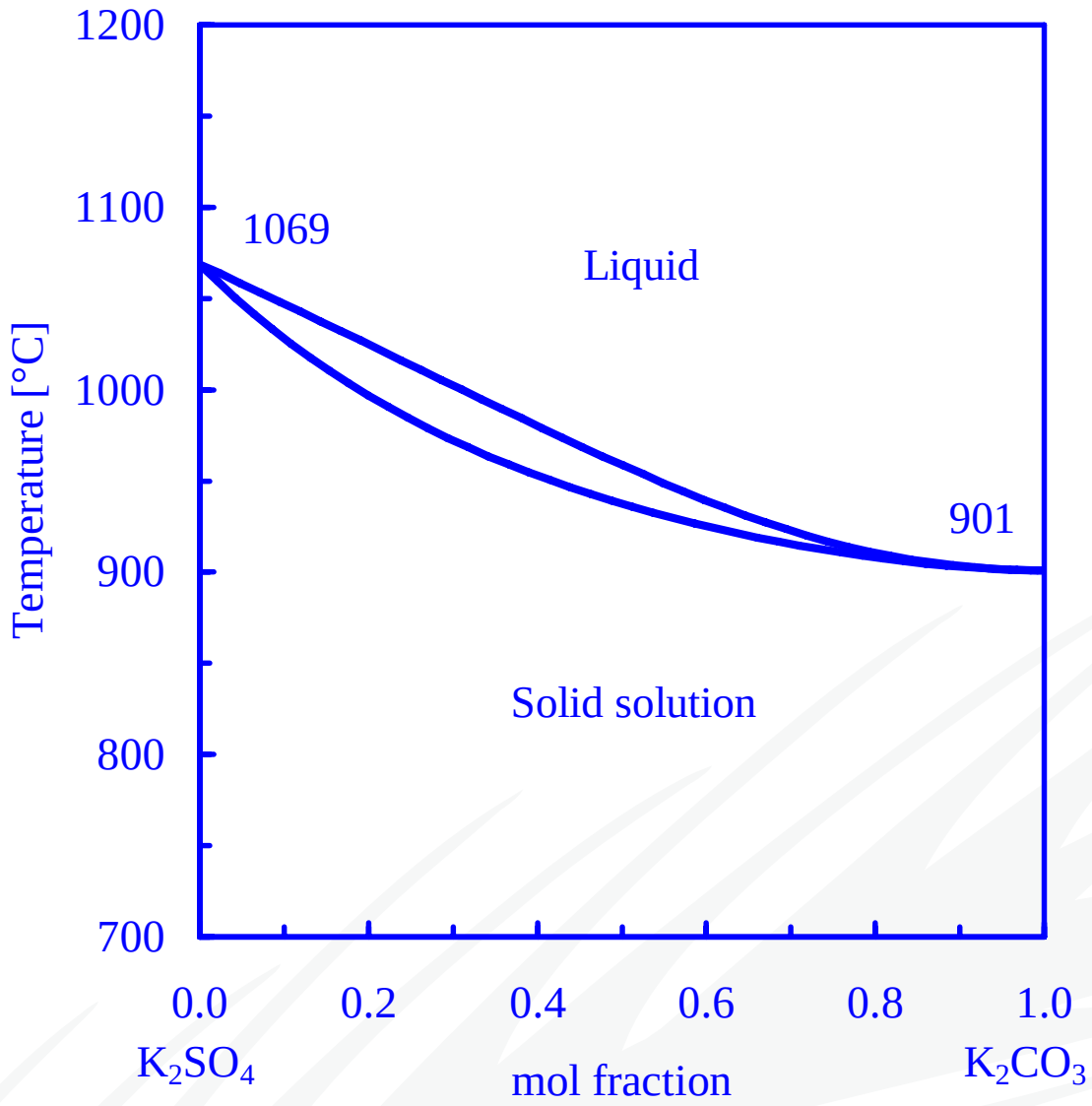
Calculation of phase diagram Na2SO4-NaCl

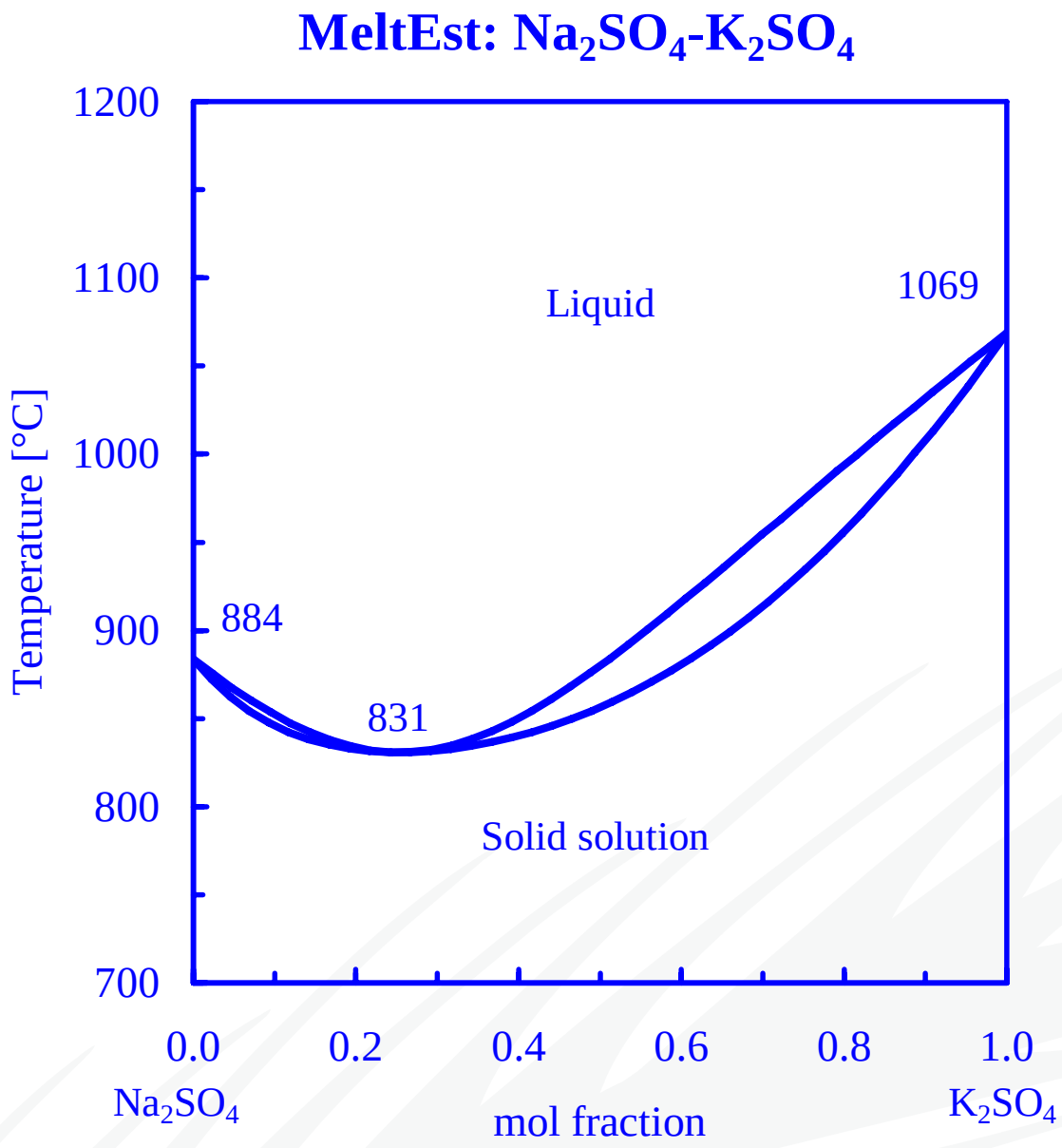


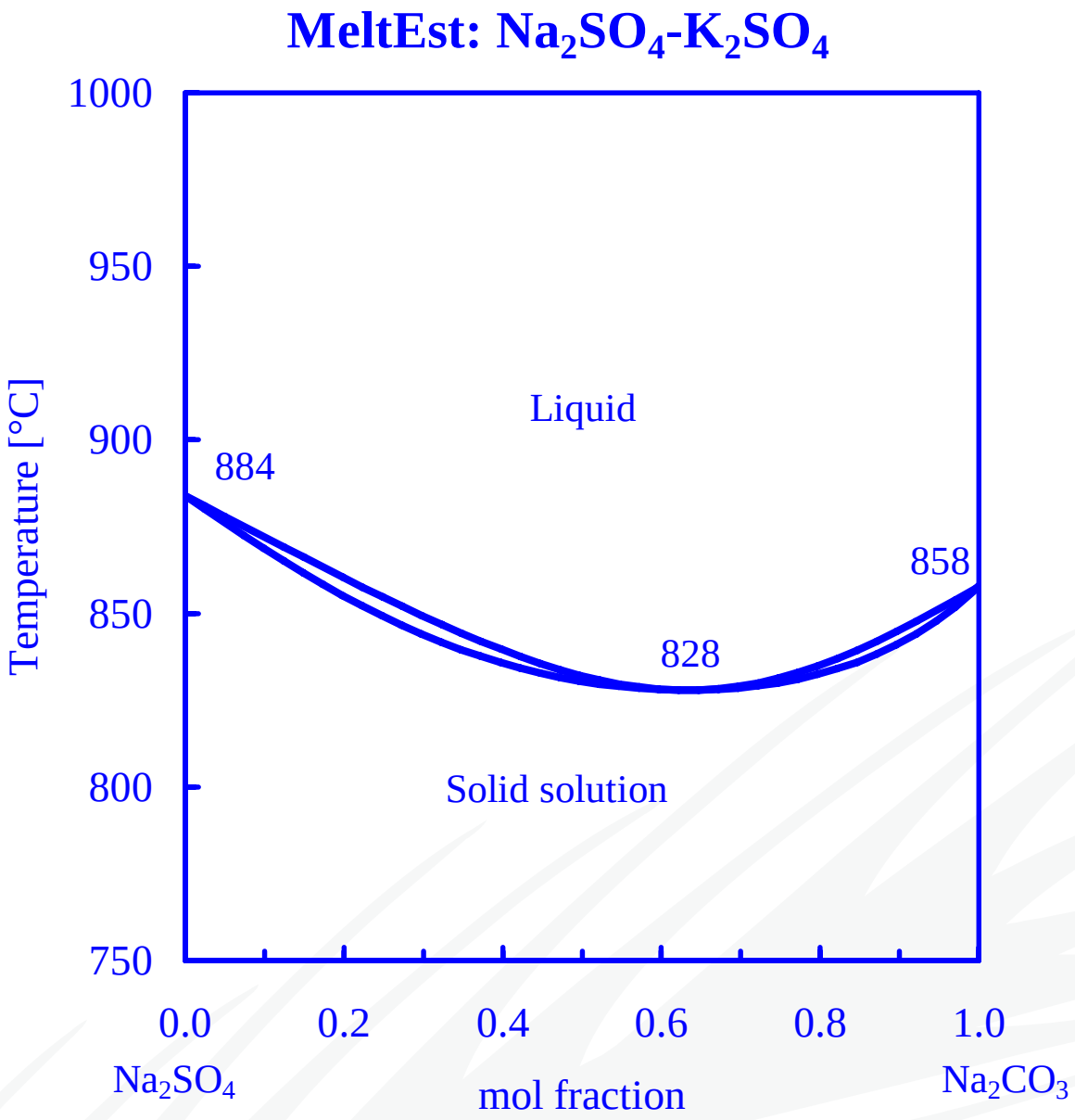
Features of two-component systems

- Components completely soluble in melt (eutectic systems)
- Components also completely soluble in each others crystalline phases (solid solutions)
- Components form intermediate compounds

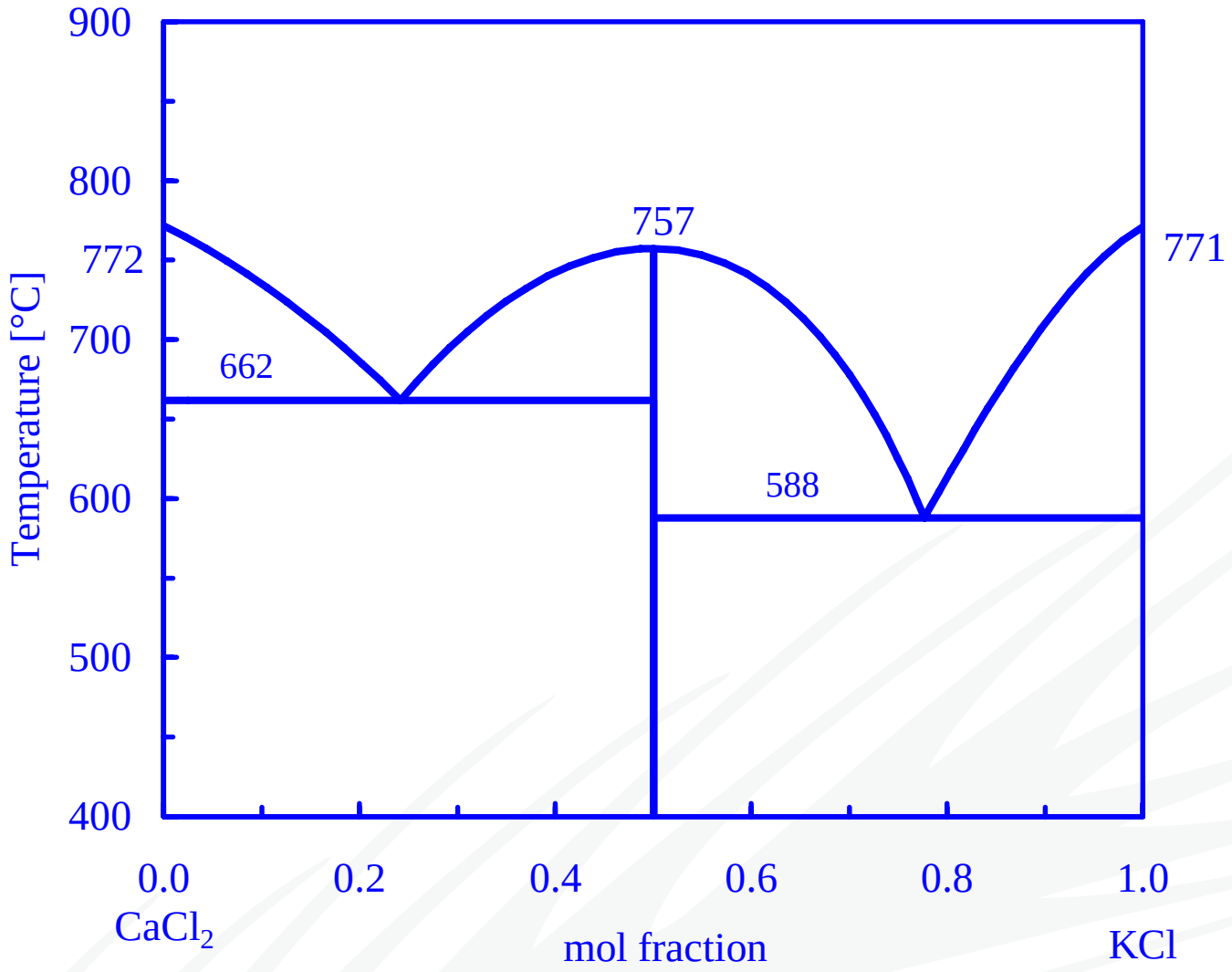
MeltEst: K_2SO_4-K_2CO_3

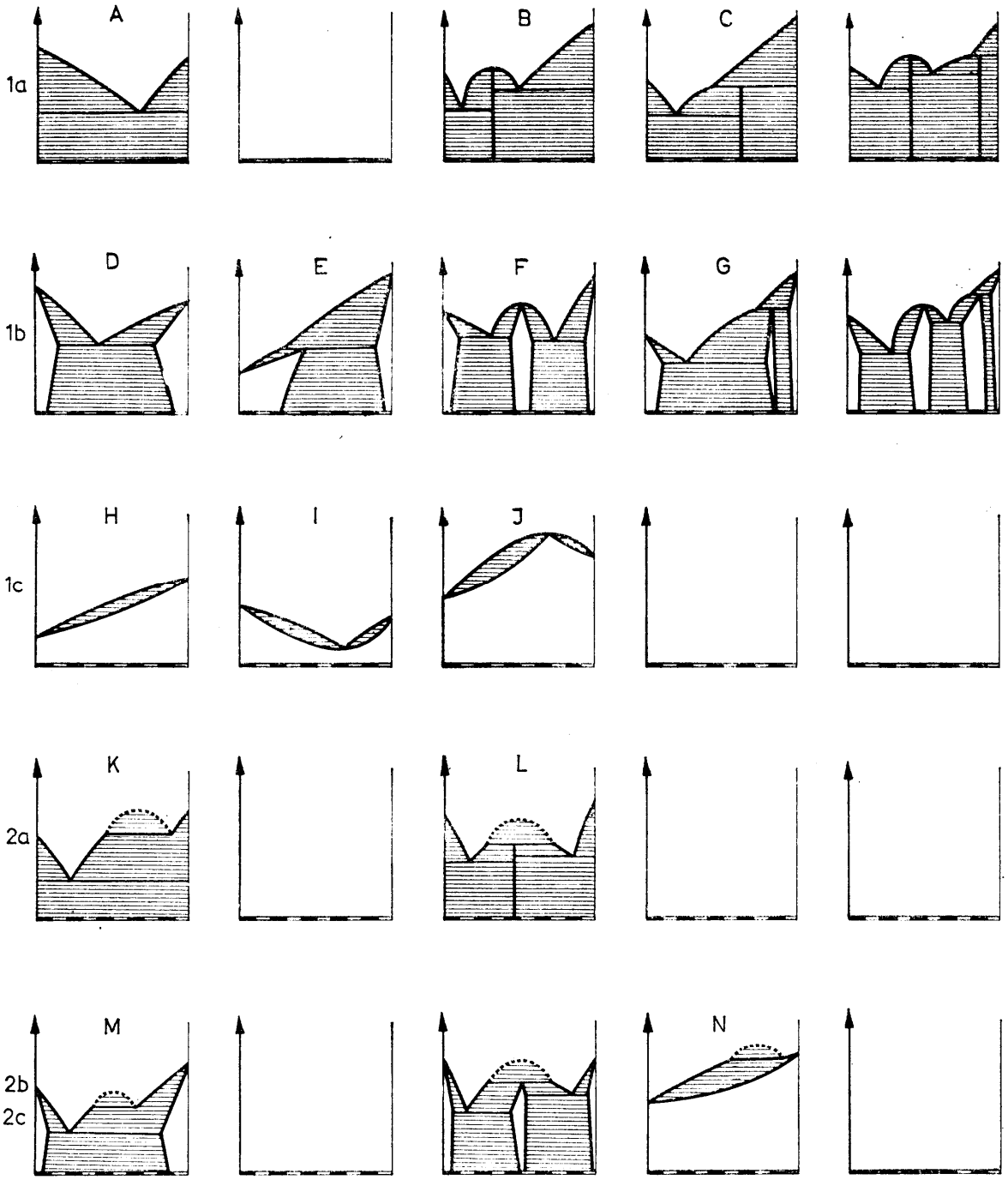


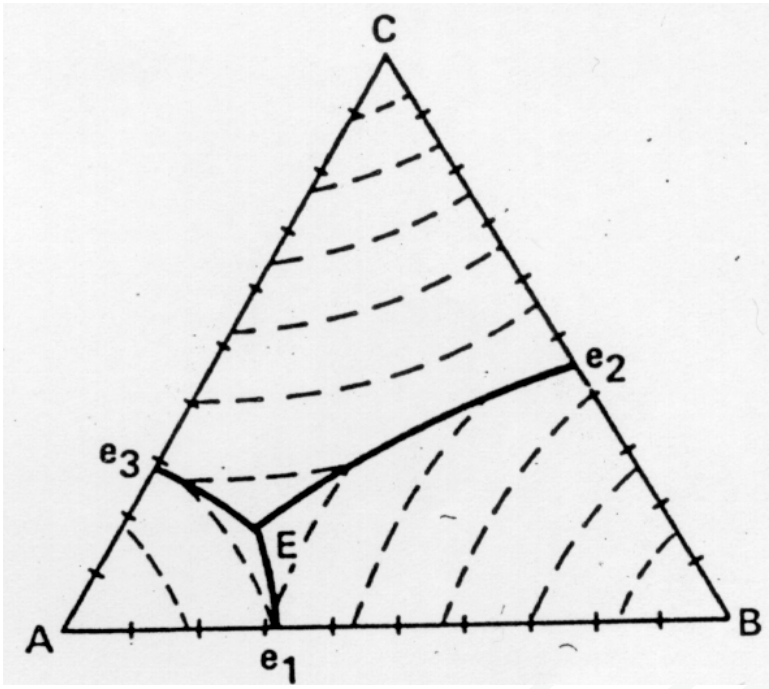

MeltEst: Na2SO4-K2SO4
1200
1100
1000
900
800
700
Temperature [°C]
Liquid
1069
884
831
Solid solution
0.0
0.2
0.4
0.6
0.8
1.0
Na2SO4
mol fraction
K2SO4

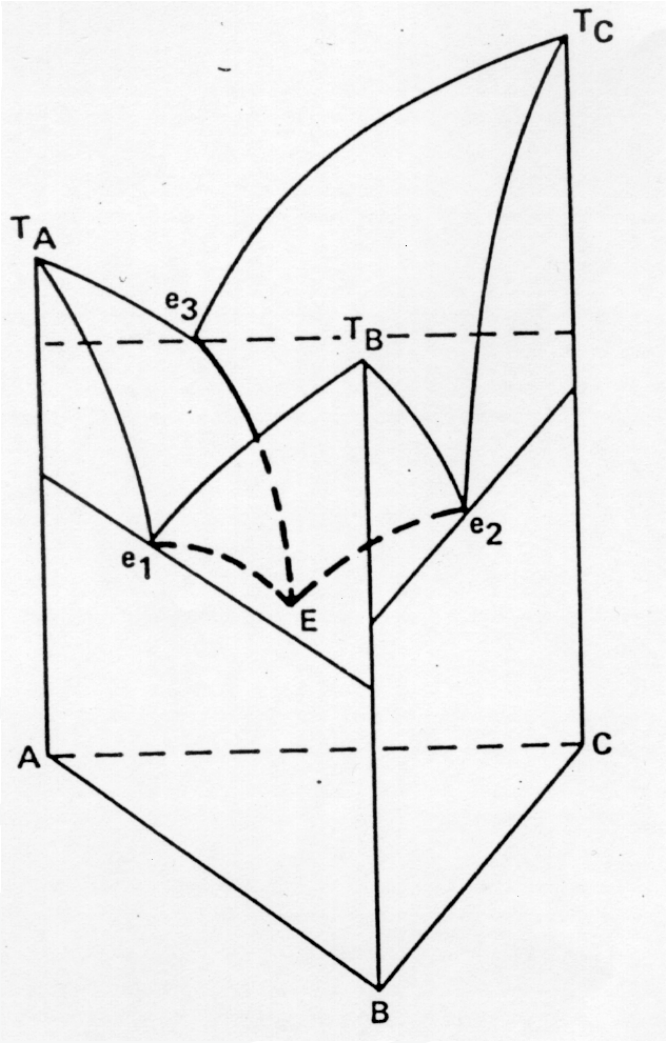

MeltEst: Na2SO4-K2SO4
1000
950
900
850
800
750
Temperature [°C]
Liquid
884
858
828
Solid solution
0.0
0.2
0.4
0.6
0.8
1.0
Na2SO4
mol fraction
Na2CO3

MeltEst: $CaCl_2$-KCl




A
B
C
1a
D
E
F
G
1b
H
I
J
1c
K
L
2a
M
N
2b
2c

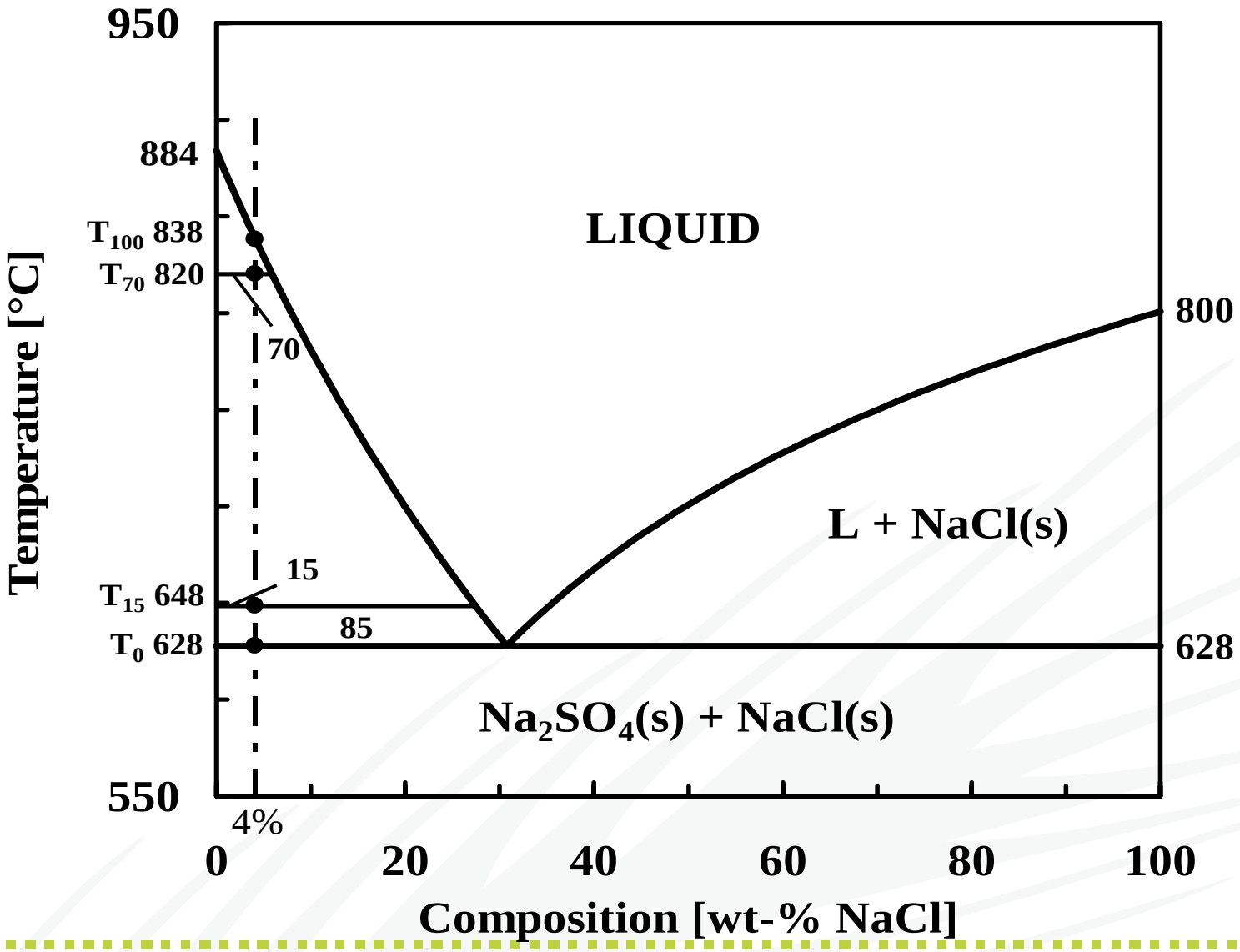




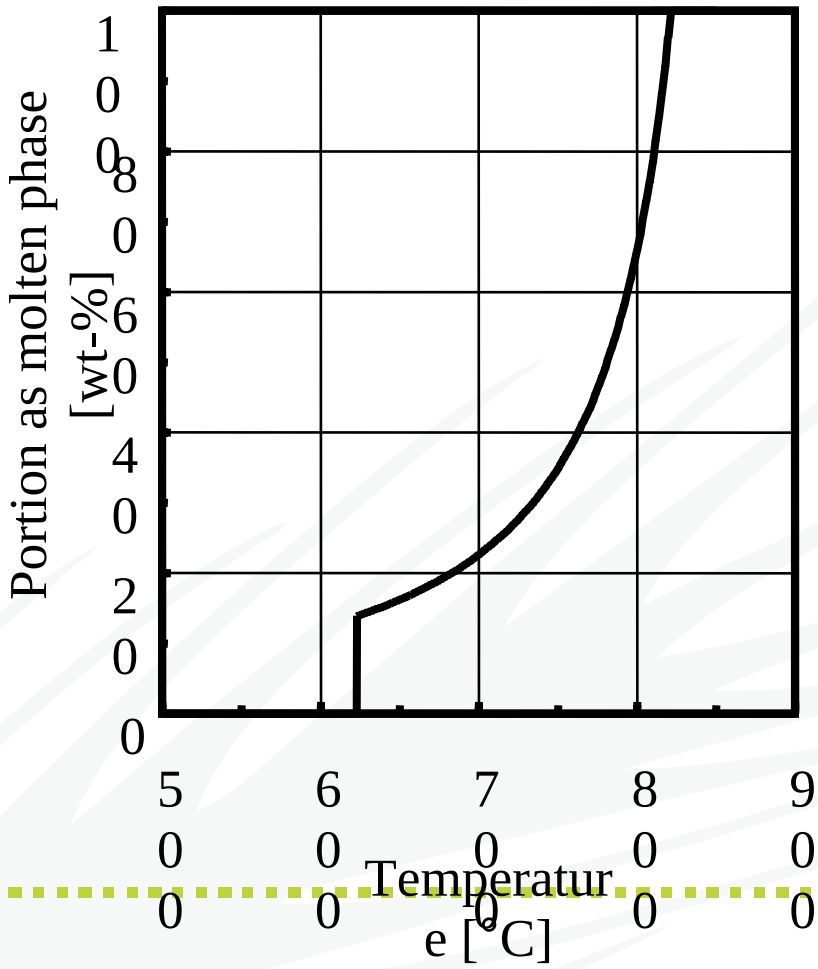
Ternary Eutectic System

Percentage of Liquid Phase

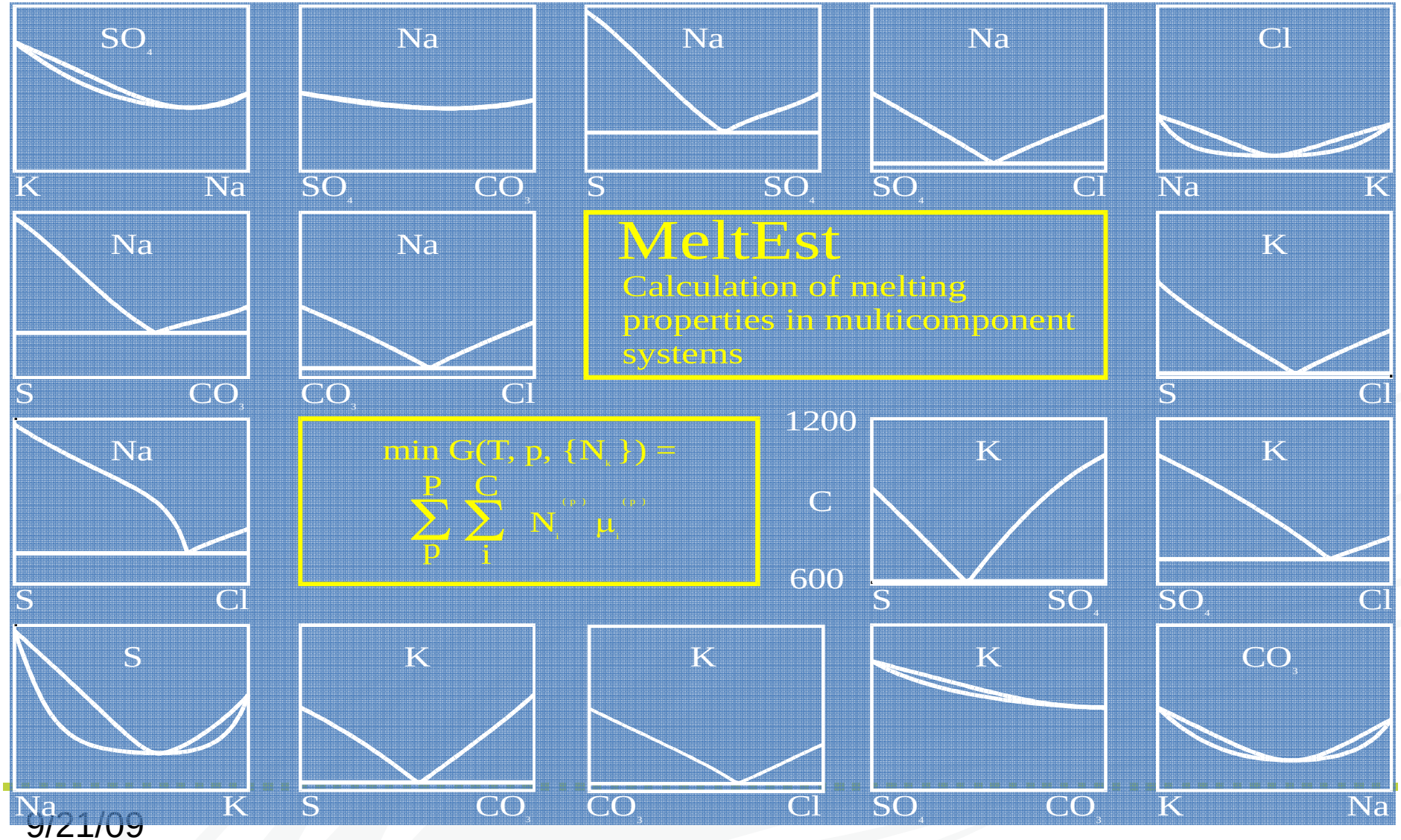
Lever rule- amount melt



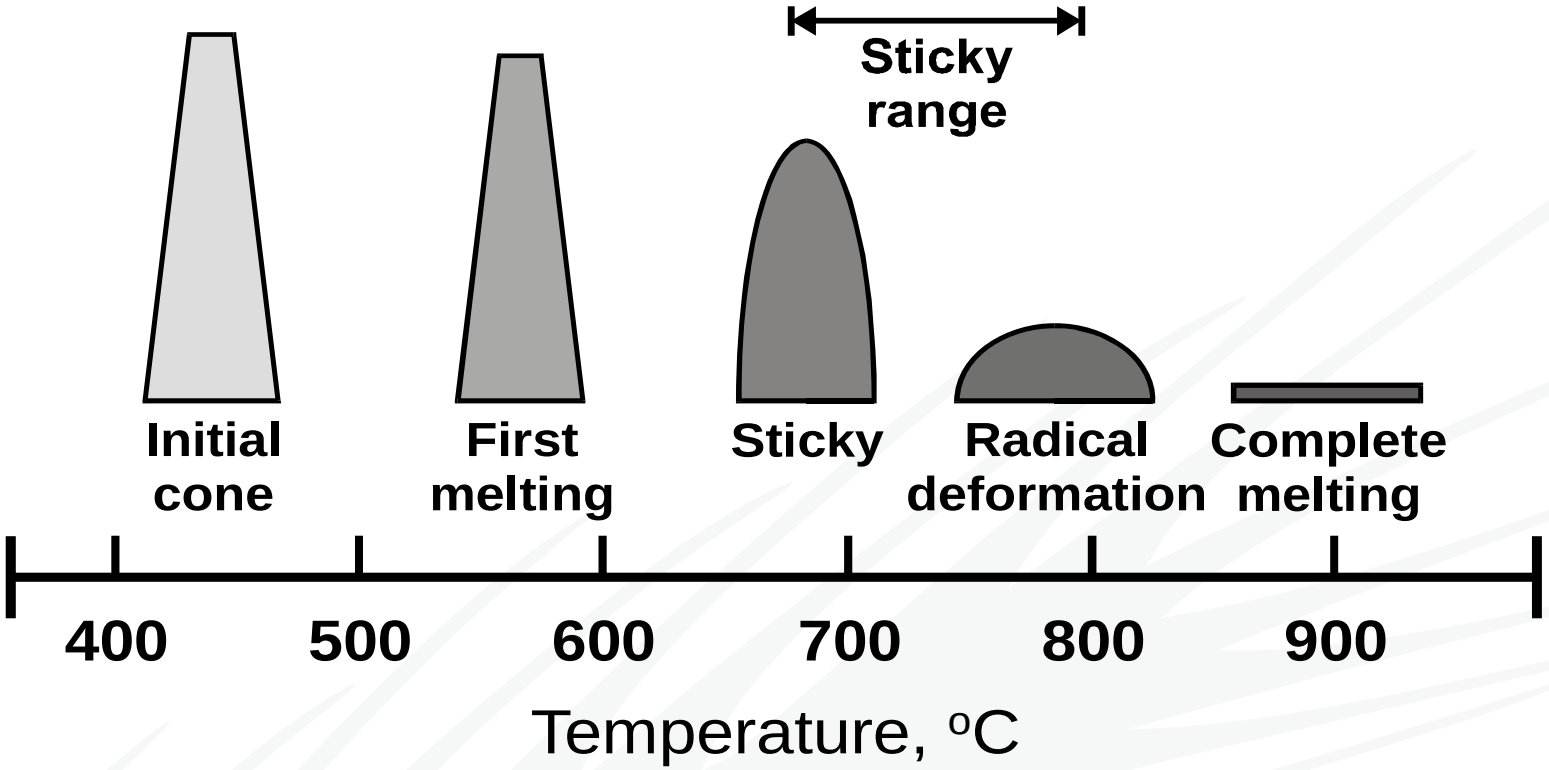
Percentage melt vs temperature
4 % NaCl - 96 %NaSO4



Alkali Salt Melting Property Predictor

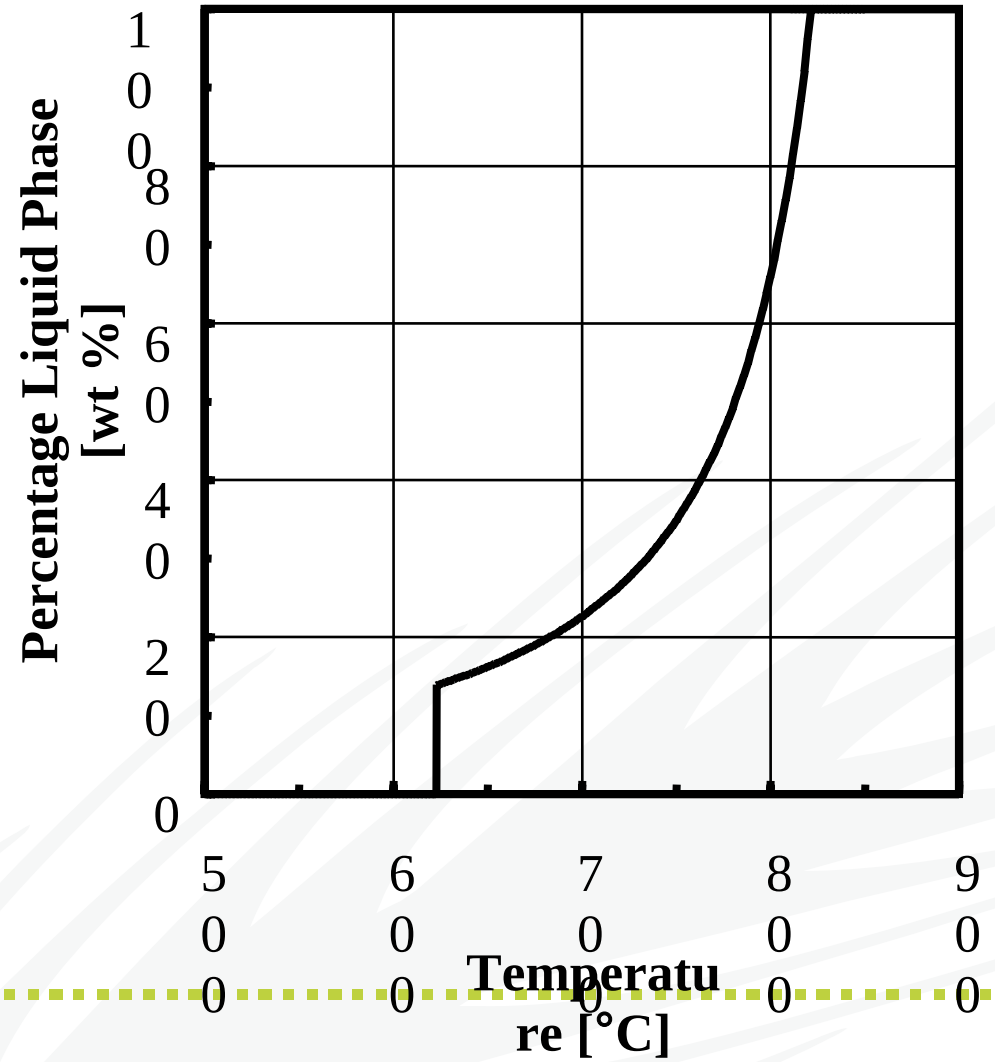


Salt Mixture Melting at Increasing Temperatures



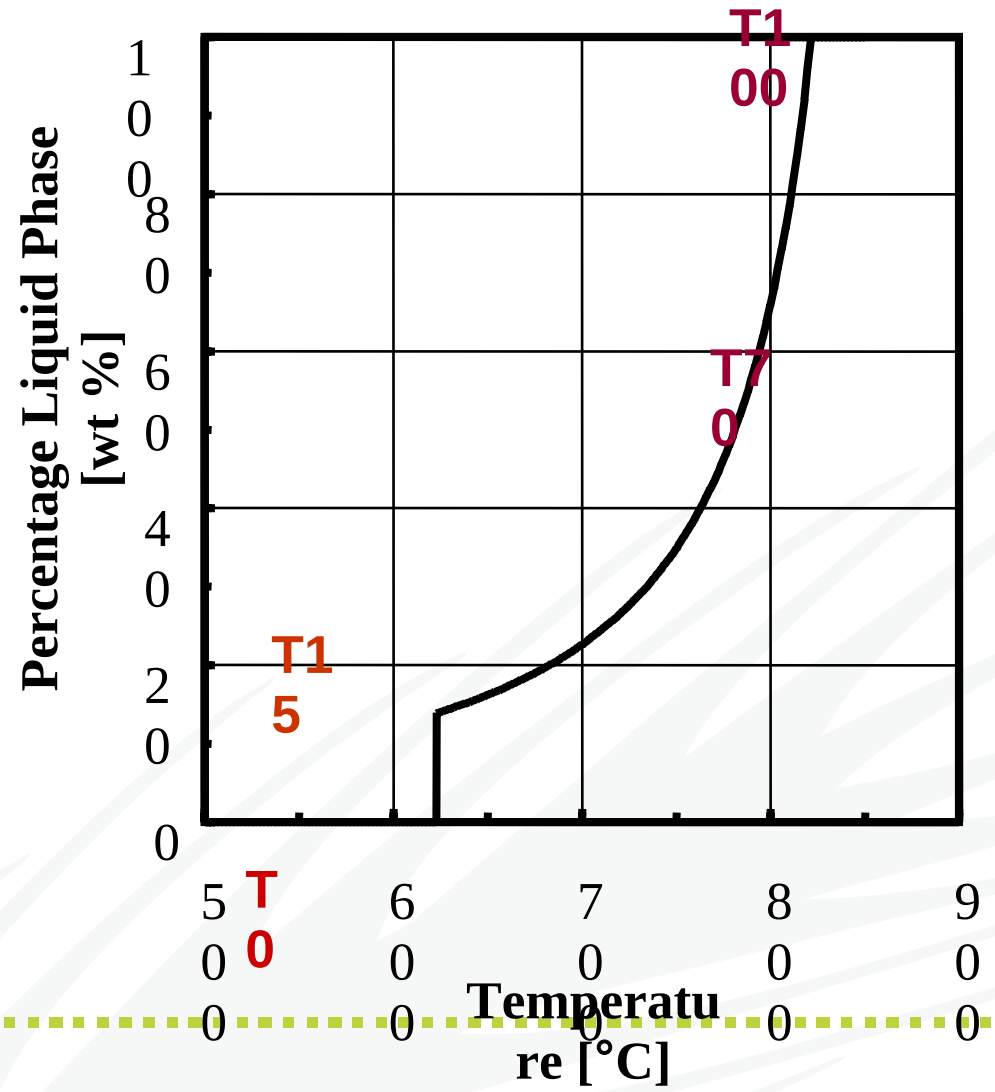
Fraction of Molten Phase vs. Temperature

Typical Superheater Deposit



Fraction of Molten Phase vs. Temperature

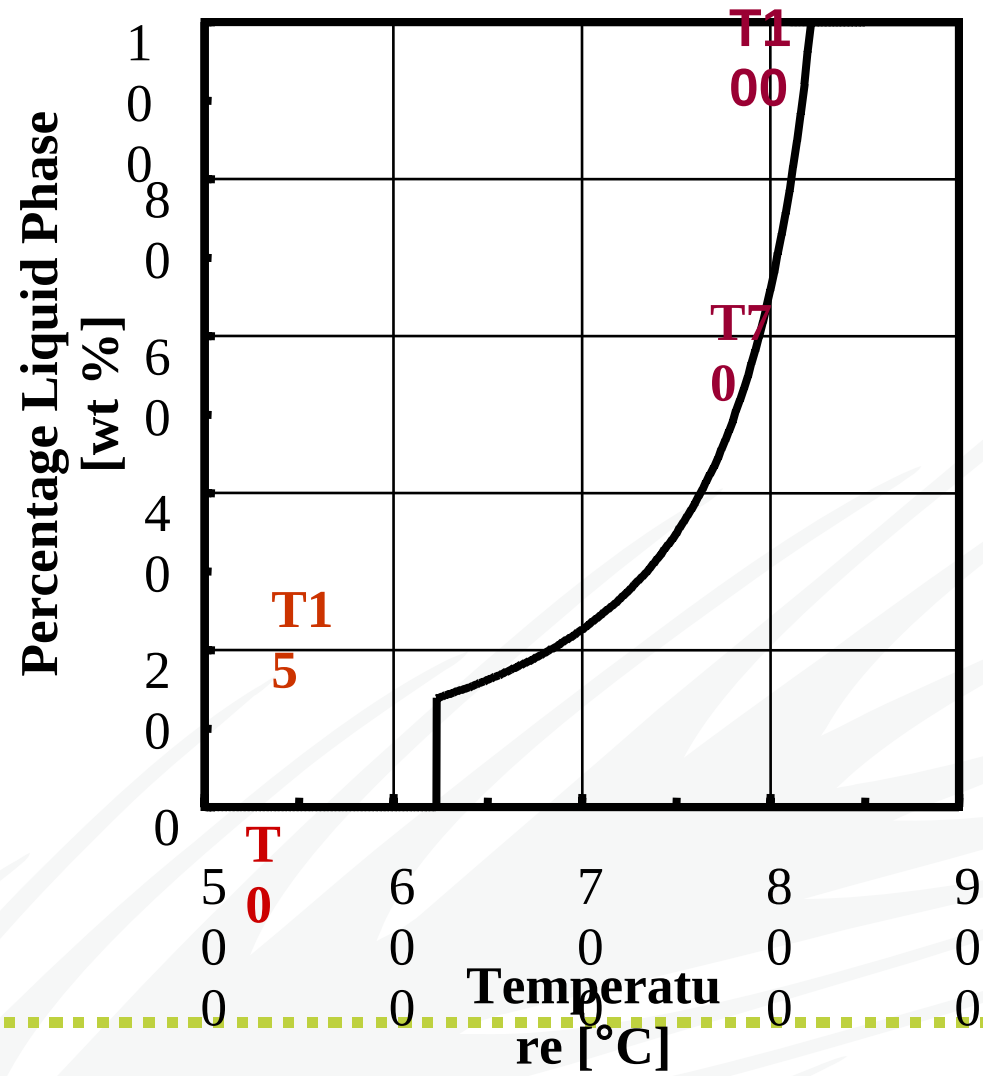
Typical Superheater Deposit



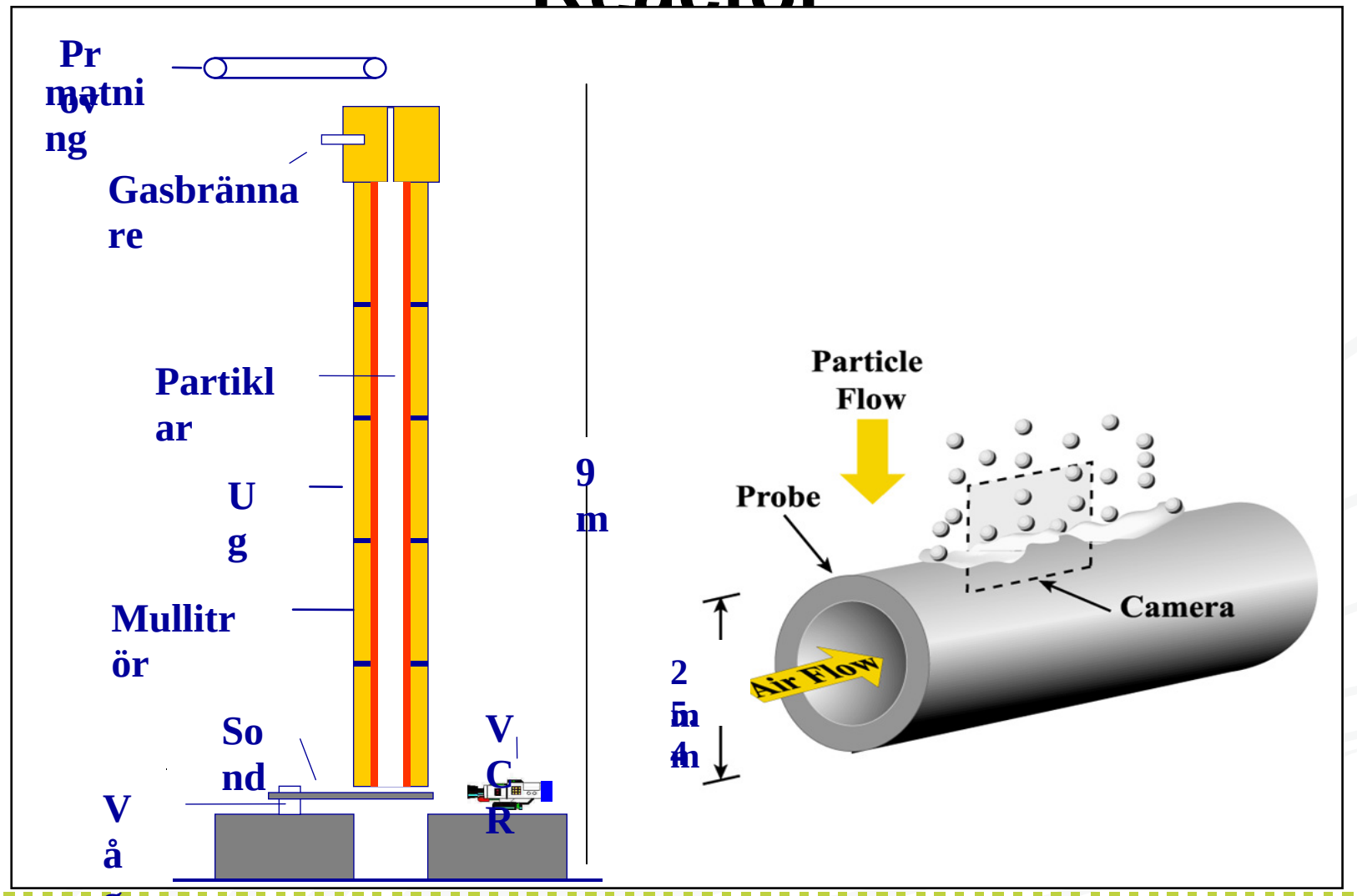
Sticky Fly Ash and T_{15}

Fraction of Molten Phase vs. Temperature

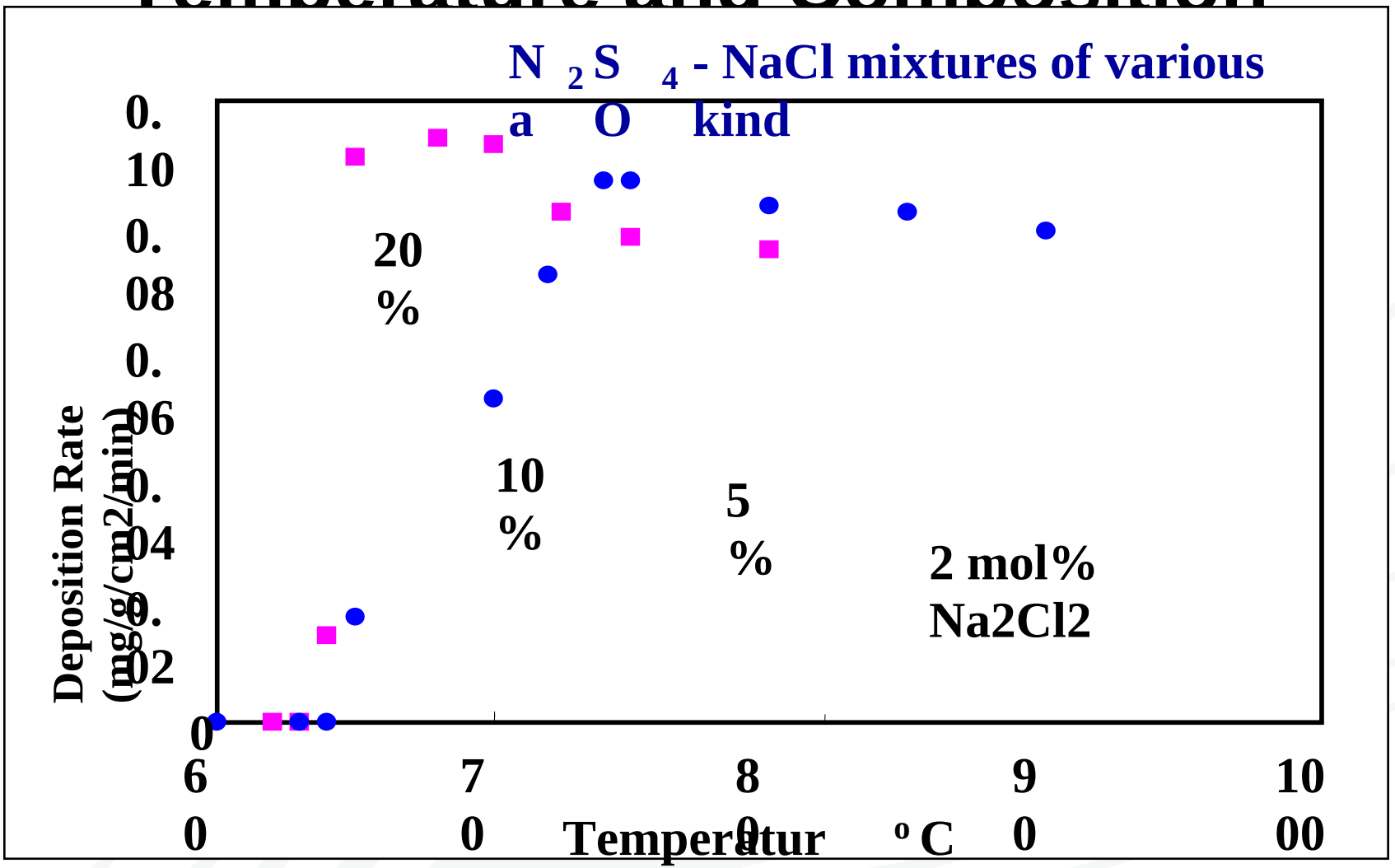
Typical Superheater Deposit



Entrained Flow Particle Reactor

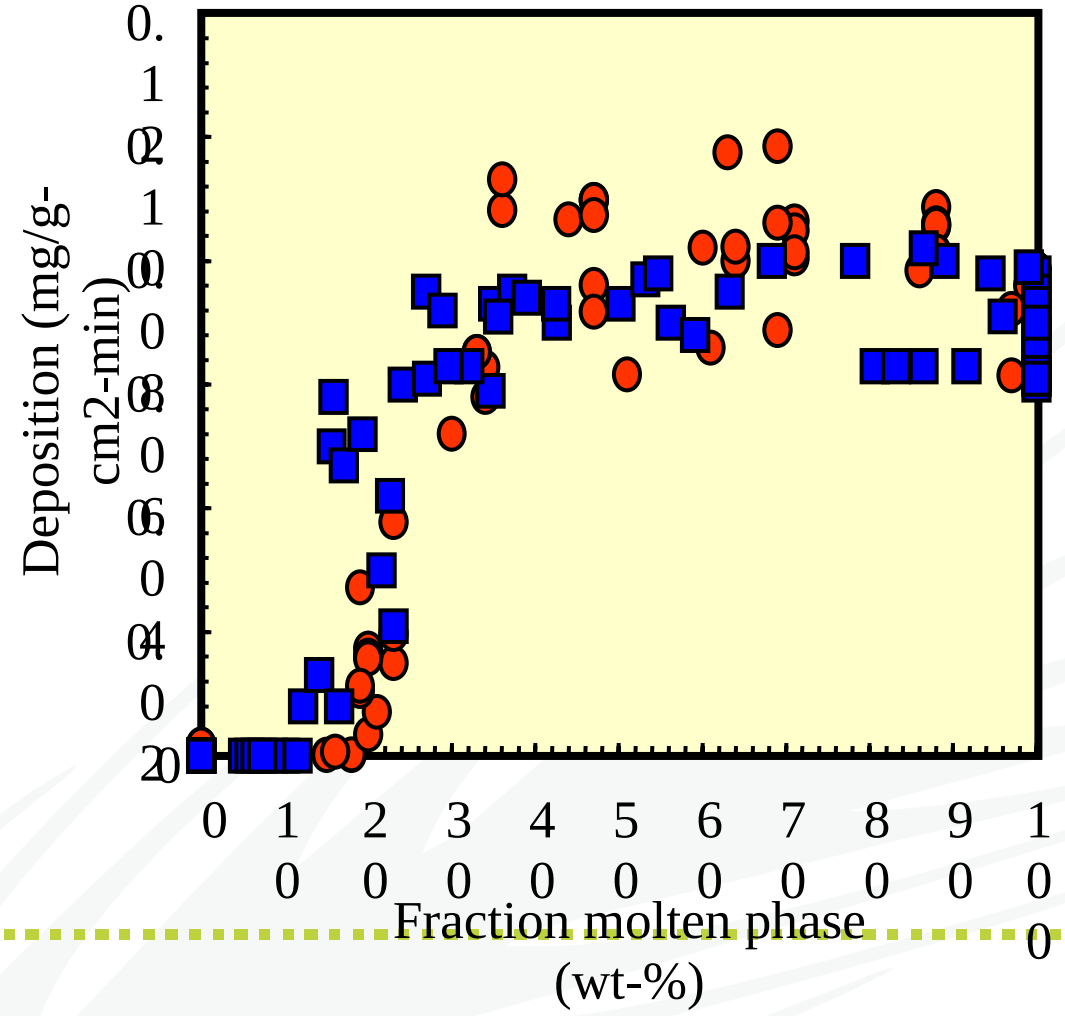


Stickiness of Salt Particles vs. Temperature and Composition



Stickiness of Partially Molten Particles

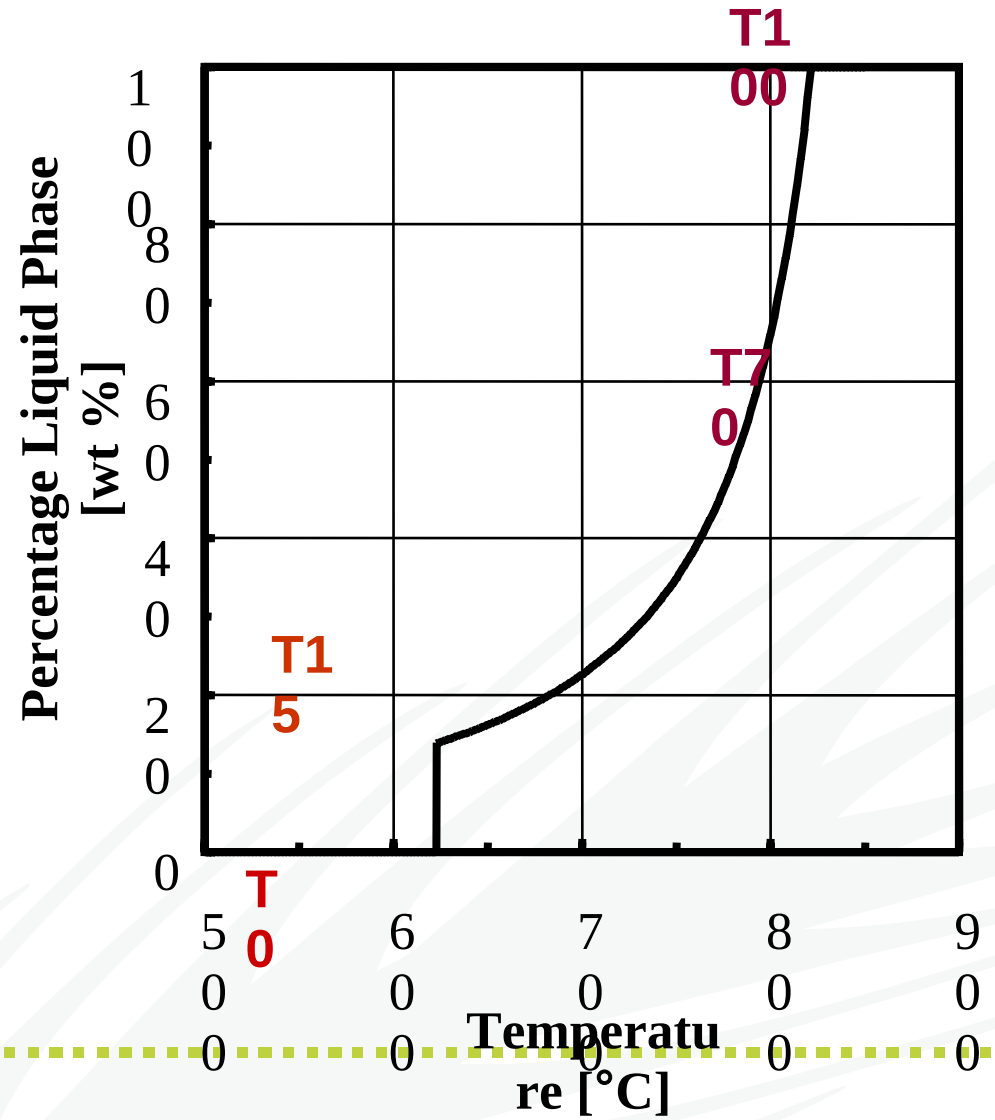
Entrained Flow Reactor Tests in Toronto



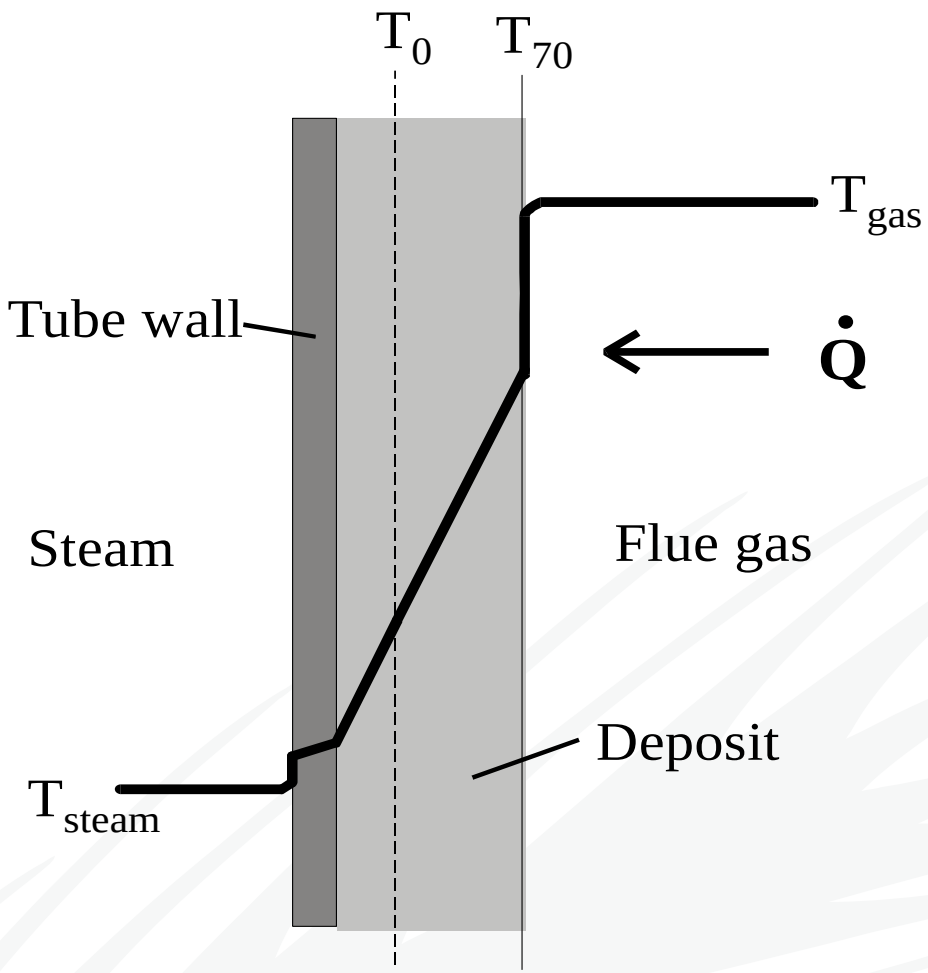
Flowing Deposits and T_{70}

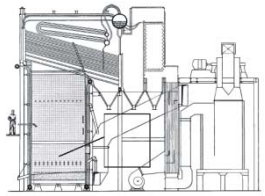
Fraction of Molten Phase vs. Temperature

Typical Superheater Deposit



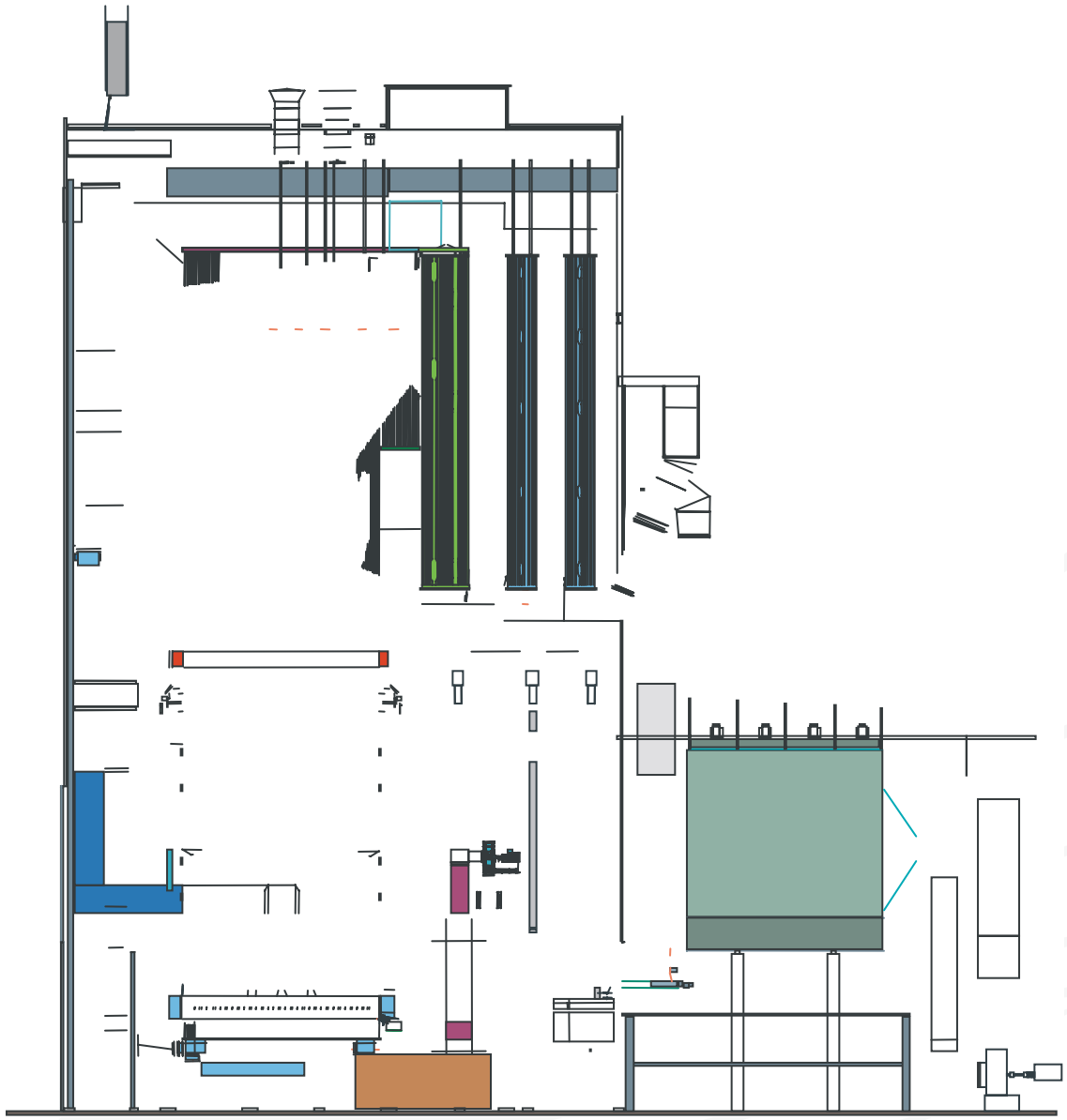
Steady state deposit thickness





15 m

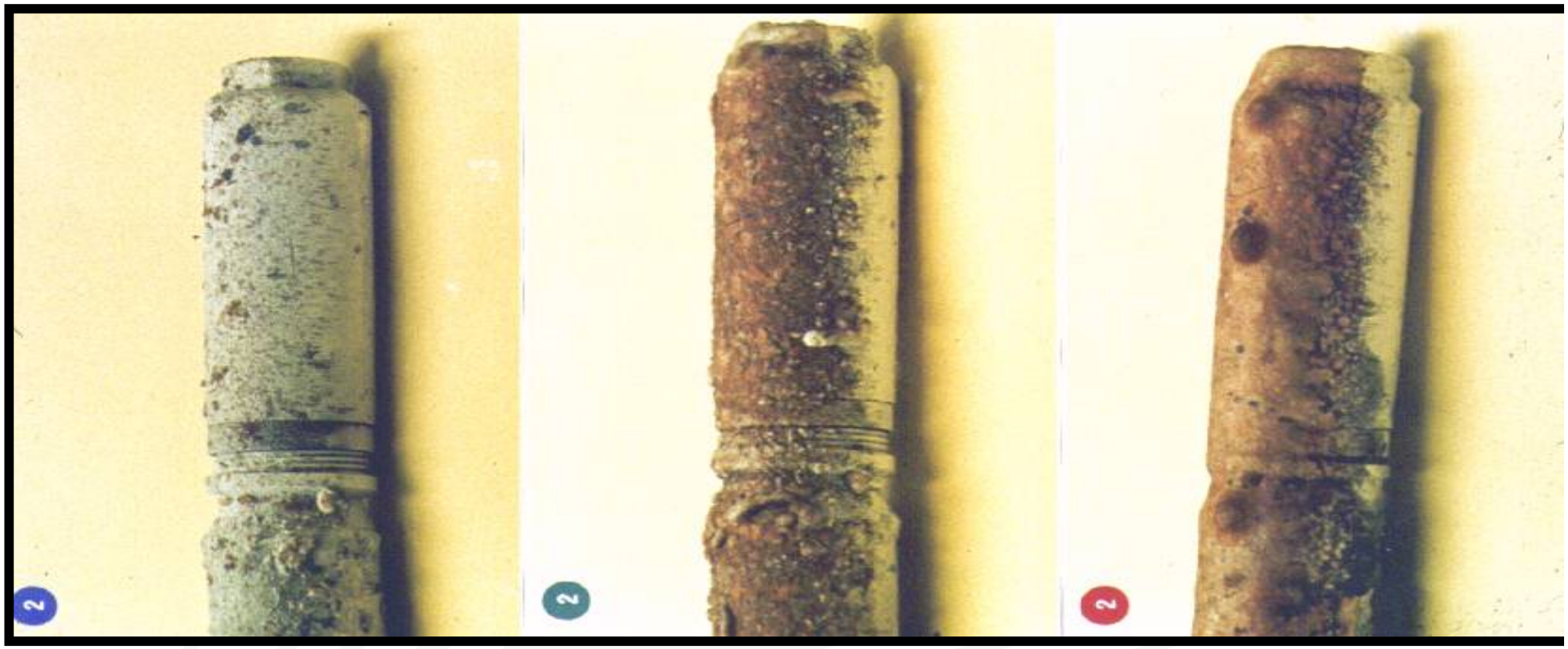
Tomlinson Boiler, 1937



85 m

Wisaforest, 2004

Probe samples

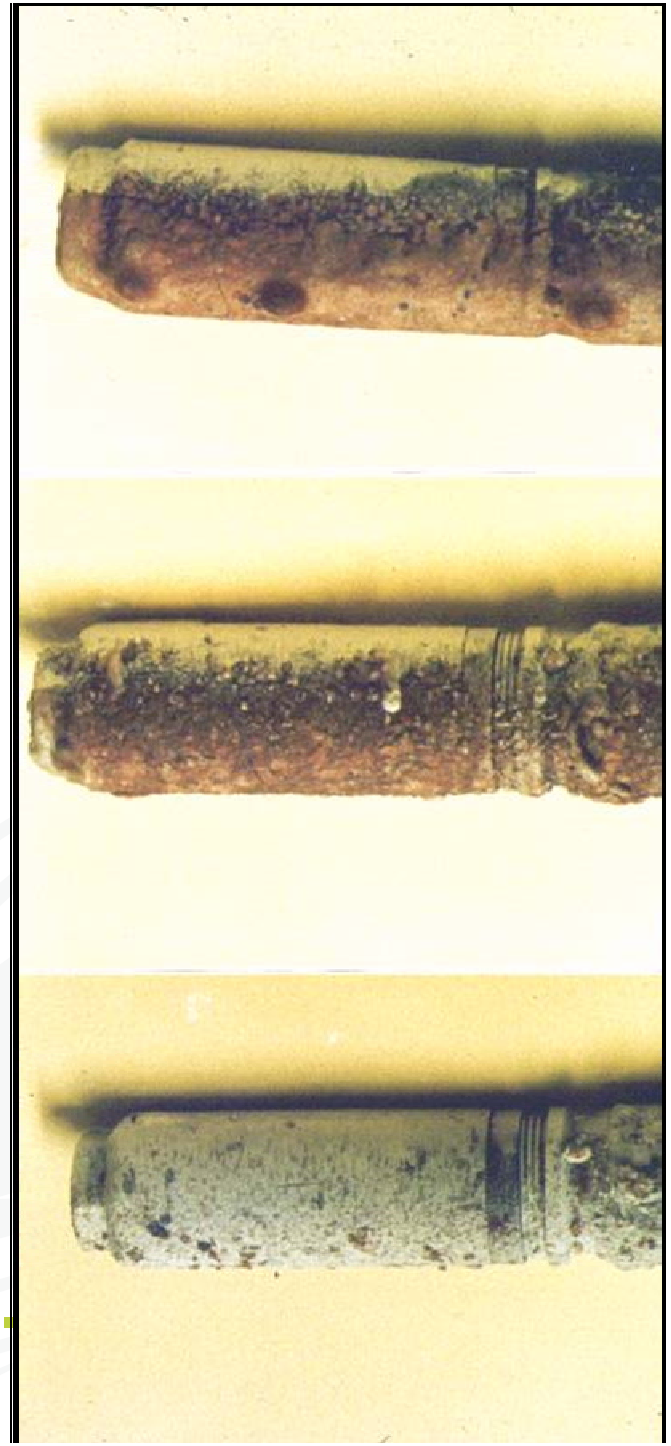


Air Cooled Probes after Exposure in Flue Gases

180 min

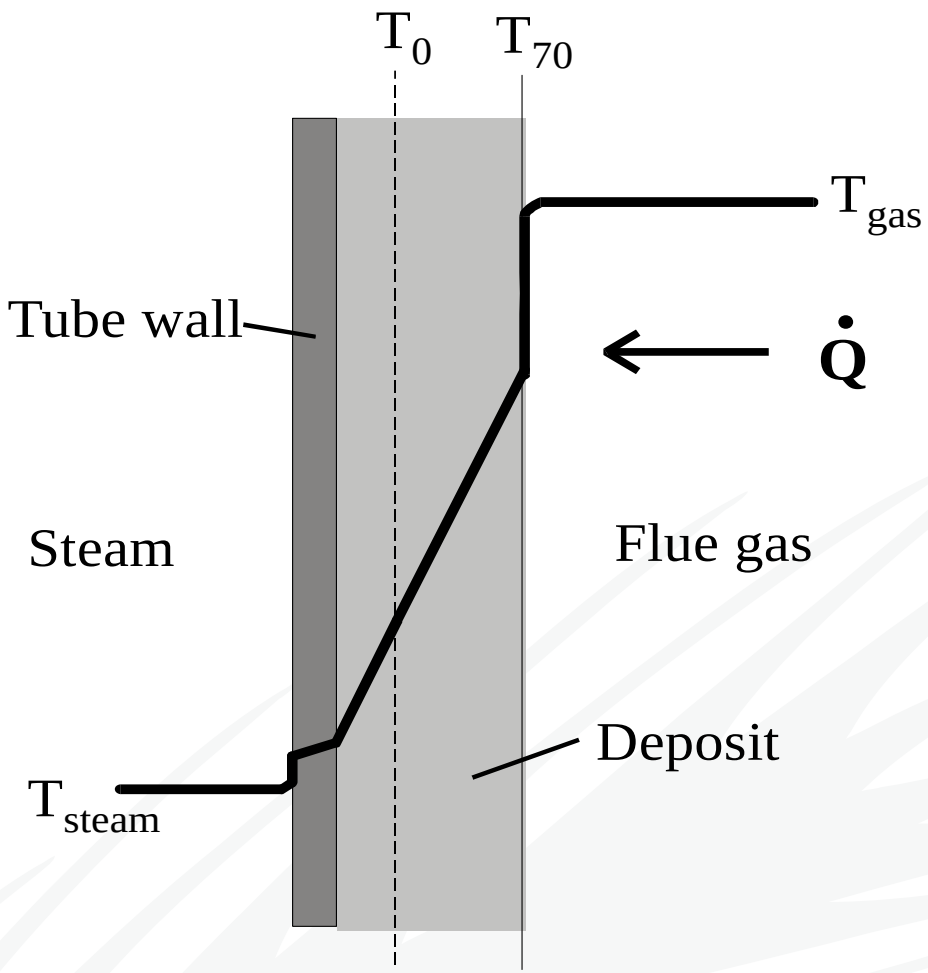
90 min

15 min

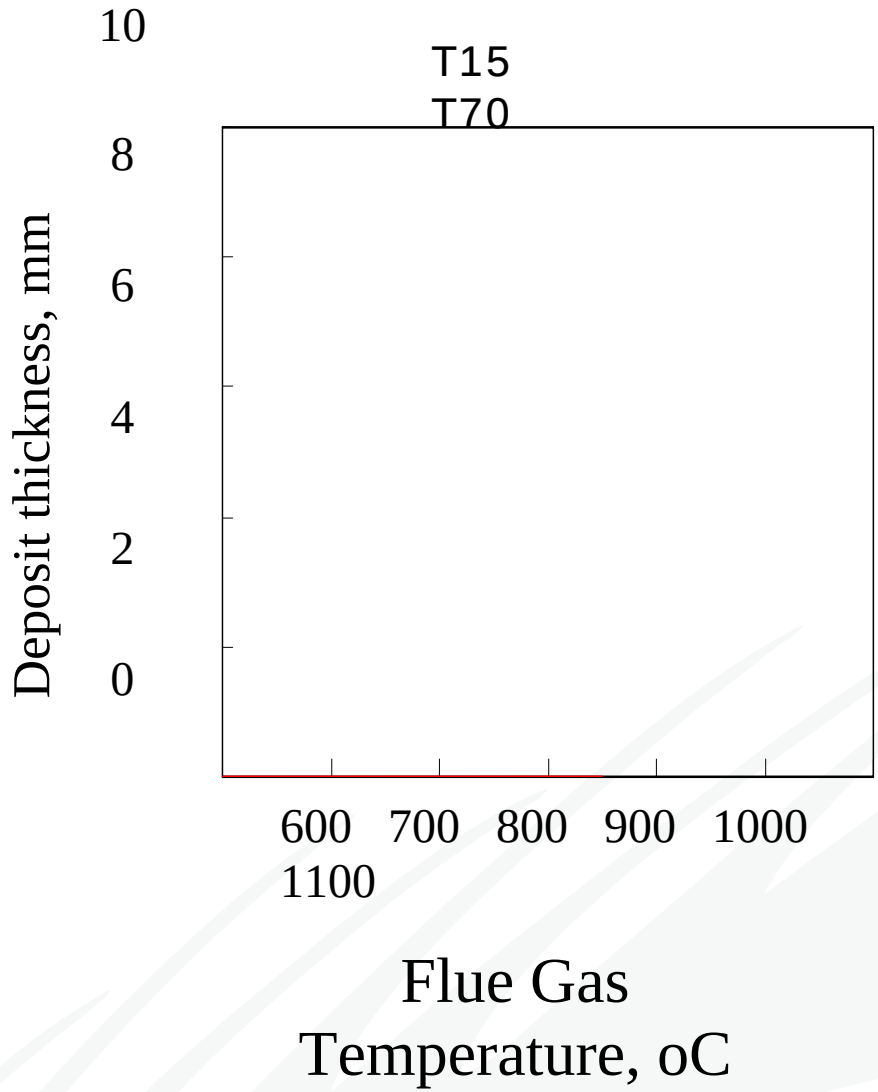


Probe Surface Temp 500 C
Flue Gas Temp 950 C

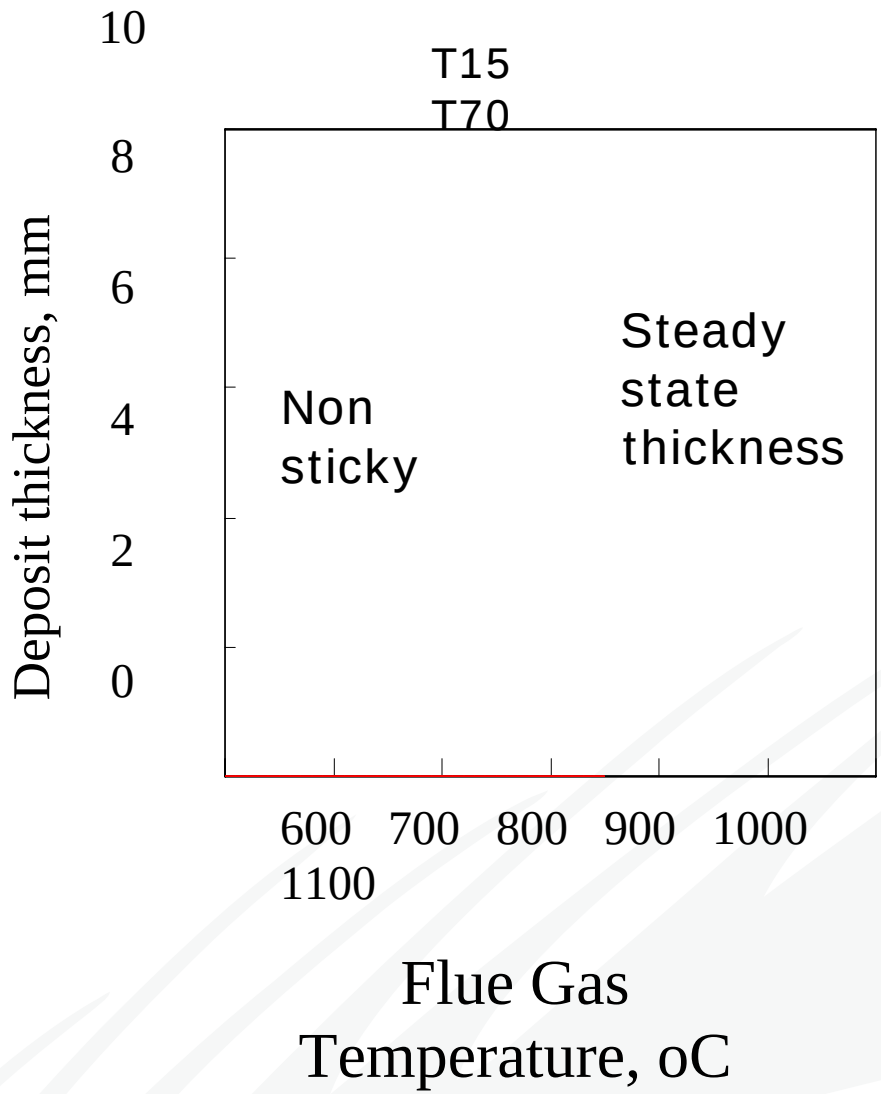
Steady state deposit thickness

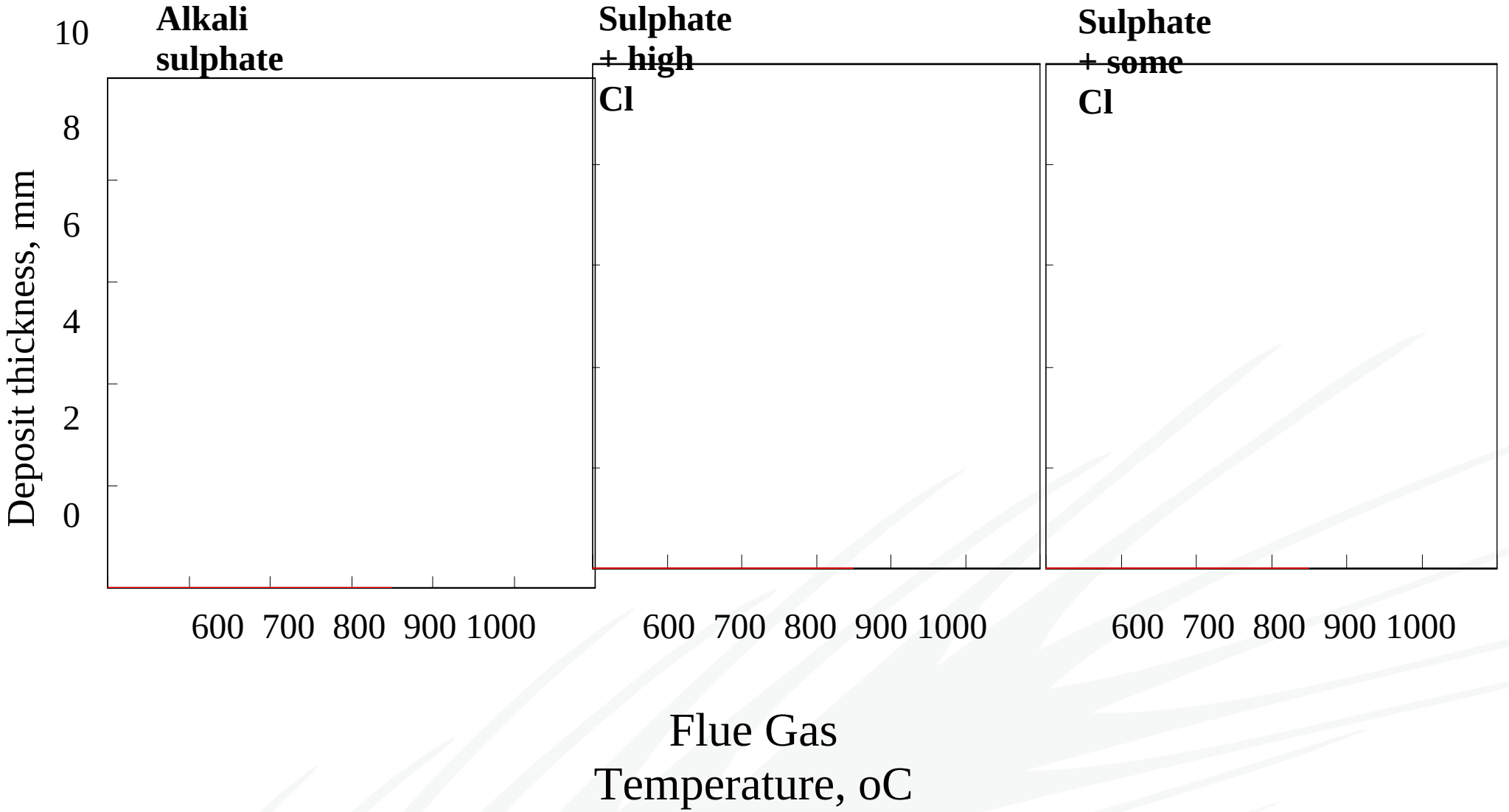


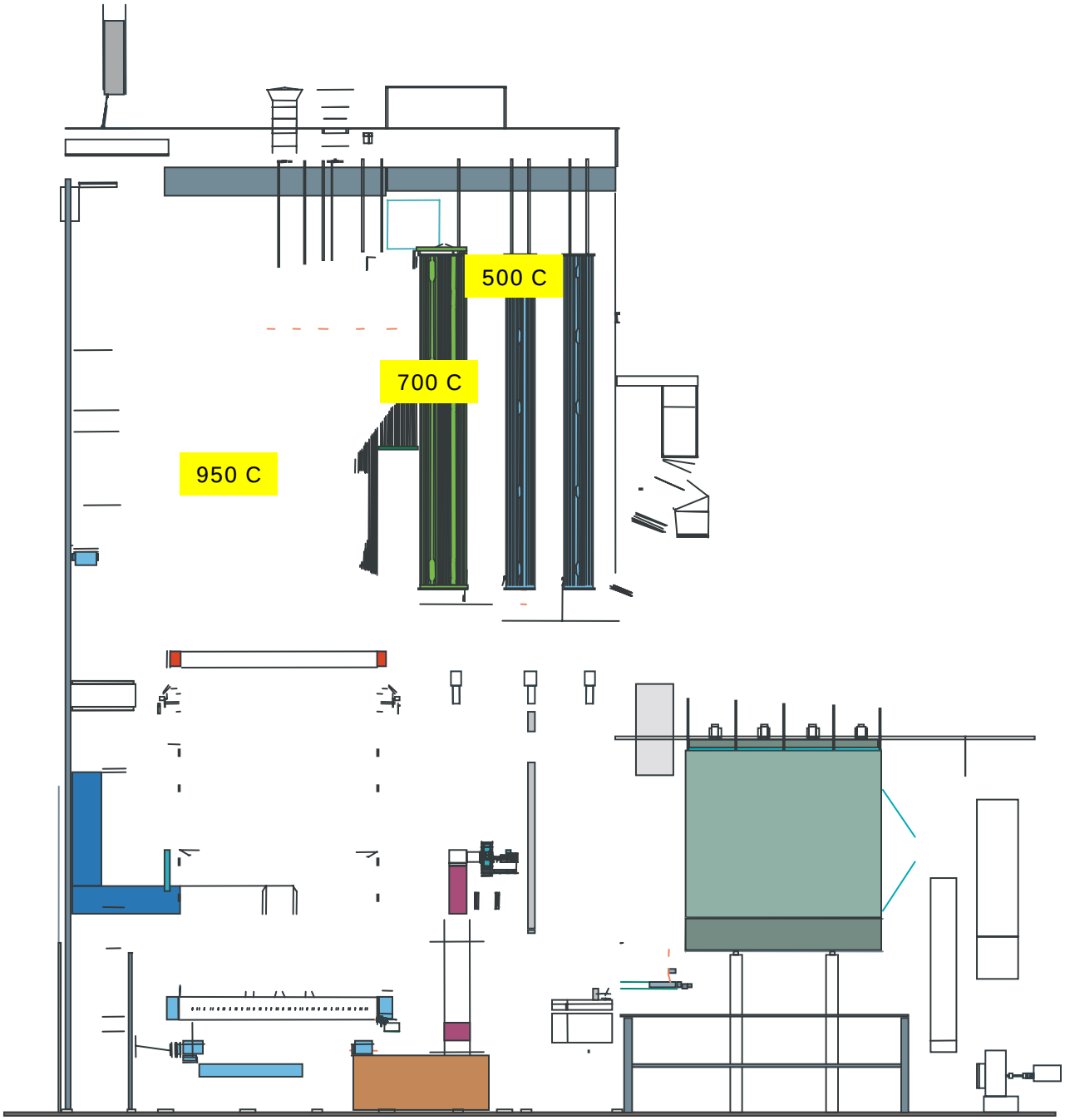
Deposit Thickness vs. Flue Gas Temperature



Deposit Thickness vs. Flue Gas Temperature

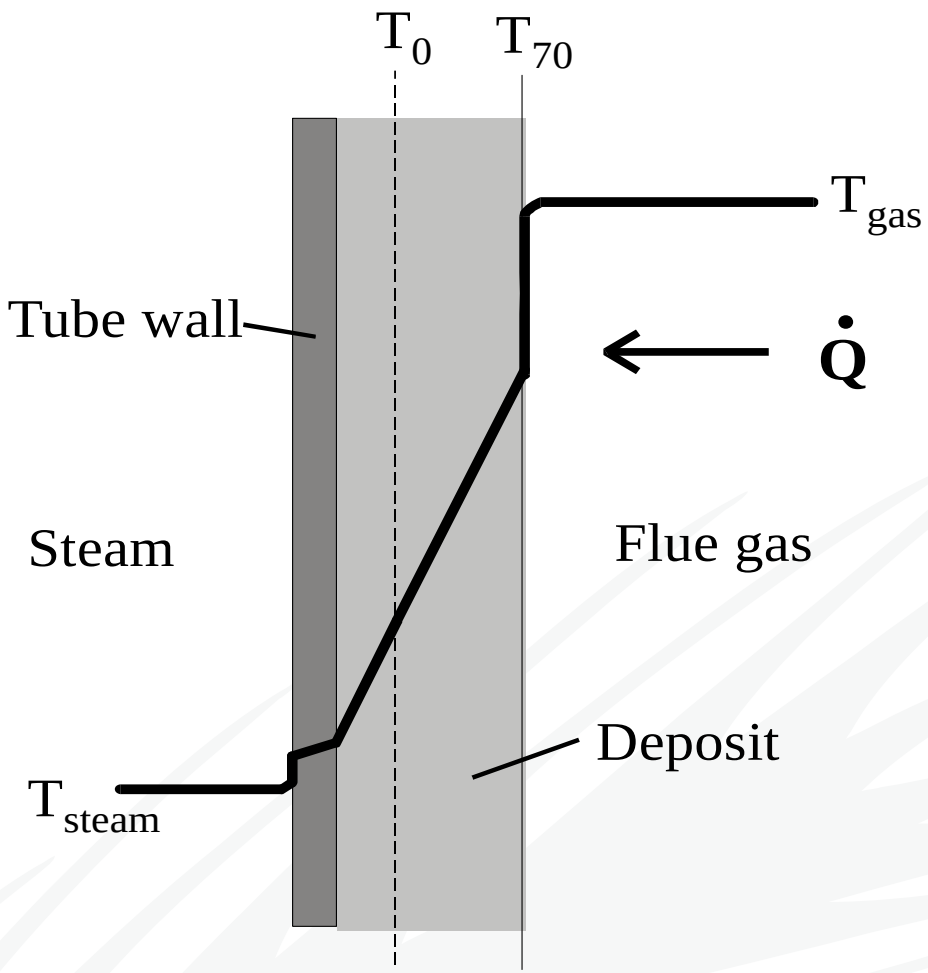



Alkali sulphate
Sulphate + high Cl
Sulphate + some Cl
Deposit thickness, mm
10
8
6
4
2
0
600 700 800 900 1000
600 700 800 900 1000
600 700 800 900 1000
Flue Gas Temperature, oC


500 C
700 C
950 C

High Temperature Corrosion and T_0

Steady state deposit thickness



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