

The influence of aerosol particles on the melting behavior of ash deposits in biomass fired boilers

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CONCLUSIONS

- **Alkali chloride in ash and deposits gives first melting temperature around 550°C.**
- **Lead and zinc together with alkali chlorides decrease the first melting temperature further to around 200°C.**
- **The amount of melt as a function of composition and temperature can be estimated using theoretical methods.**

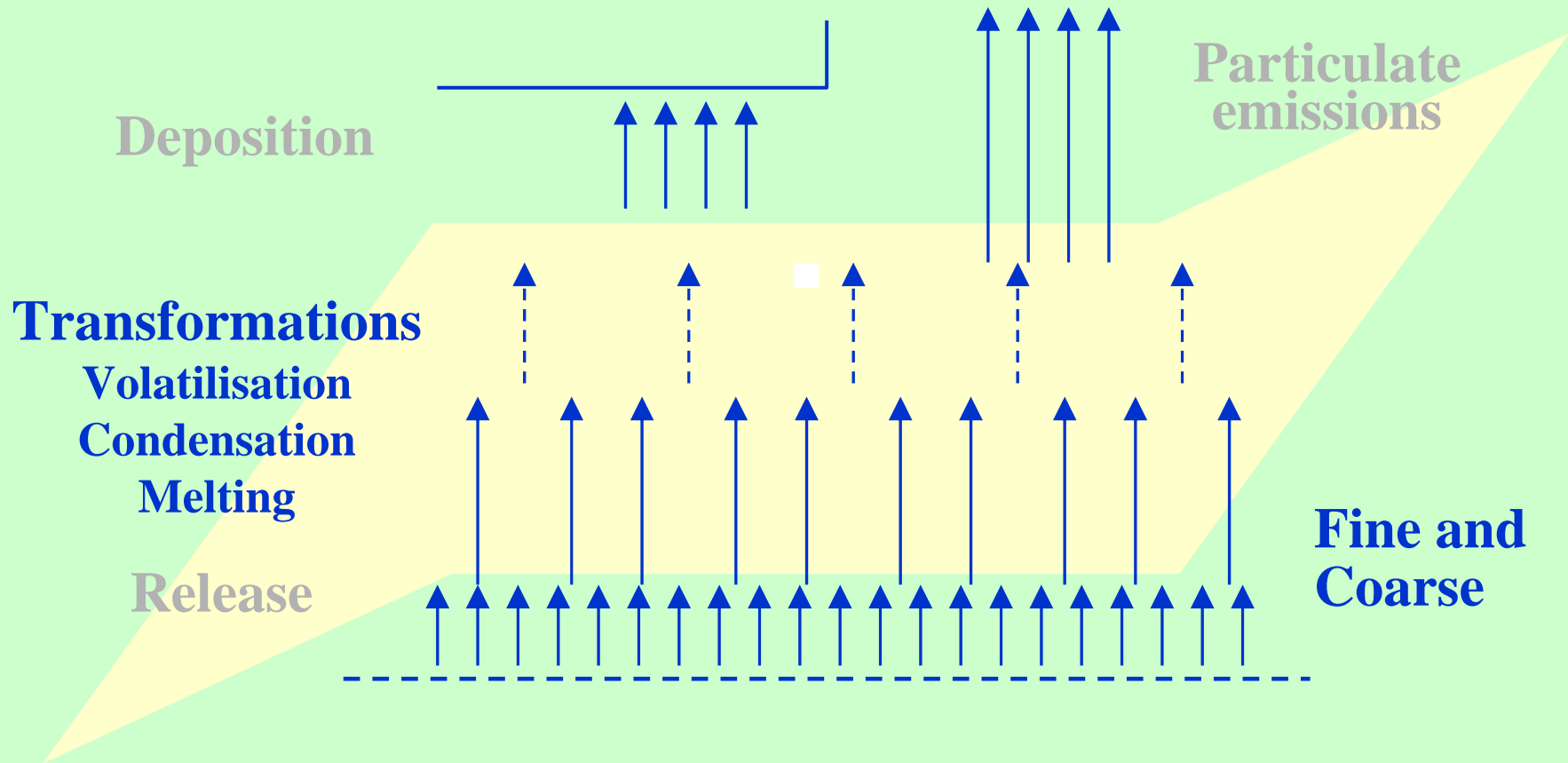
OUTLINE

- **Background**
- **Melting properties of salt mixtures**
- **Estimation of ash fraction composition**
- **Melting of ash fractions**
- **Influence of lead and zinc on melting**
- **Conclusions**

BACKGROUND

- **Novel way of predicting ash behavior**
- **Advanced fuel analysis**
- **Basic chemistry knowledge**
- **Chemical thermodynamic modeling**
- **Submodels for other models**

Ash reactions in boiler flue gases



MELTING OF SALT MIXTURES

- Pure melting points
- Stepwise melting
- Characteristic temperatures
- Complex melting models

Melting temperatures

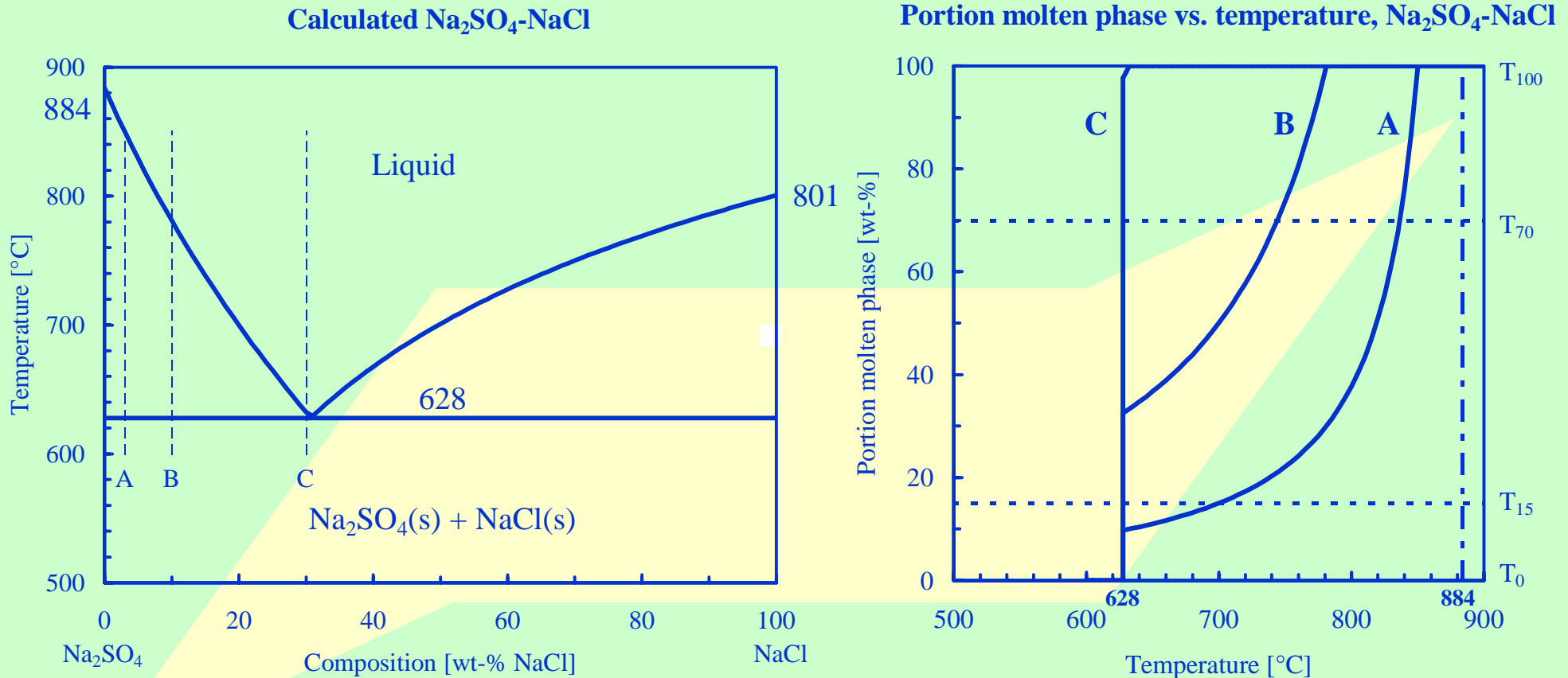
Pure compounds

PbSO ₄	1170°C
K ₂ SO ₄	1069
Na ₂ SO ₄	884
NaCl	801
KCl	771
ZnSO ₄	730
PbCl ₂	501
ZnCl ₂	318

Eutectics

PbSO ₄ -K ₂ SO ₄	814°C
PbSO ₄ -Na ₂ SO ₄	719
ZnSO ₄ -K ₂ SO ₄	566
PbSO ₄ -ZnSO ₄	674
ZnSO ₄ -Na ₂ SO ₄	485
PbCl ₂ -NaCl	444
PbCl ₂ -KCl	435
ZnCl ₂ -NaCl	294
ZnCl ₂ -KCl	288
PbCl ₂ -ZnCl ₂	243

Stepwise melting – Melting curve



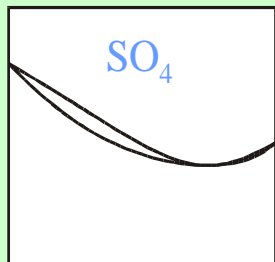
Characteristic temperatures

T_0 First melting temperature

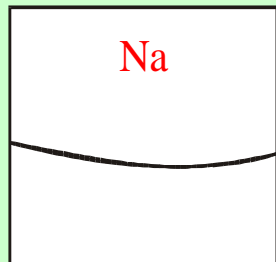
T_{15} Sticky temperature

T_{70} Flow temperature

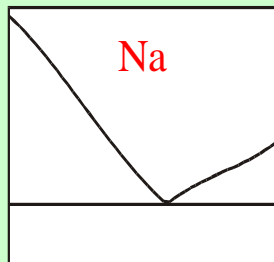
T_{100} Final melting temperature



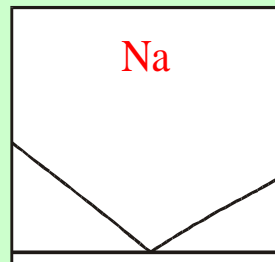
K Na



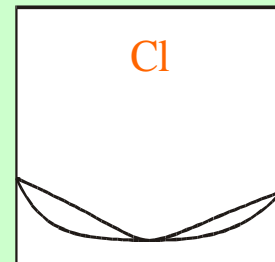
SO4 CO3



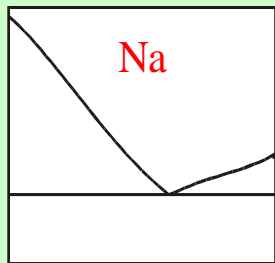
S SO4



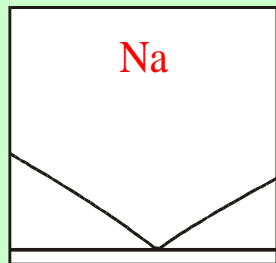
SO4 Cl



Na K

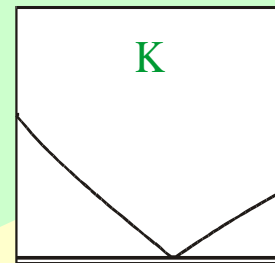


S CO3

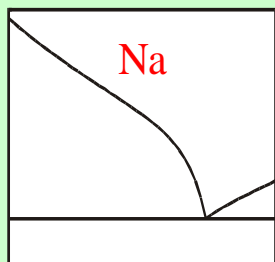


CO3 Cl

Meltest
Calculation of melting properties in multicomponent systems



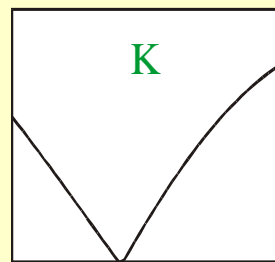
S Cl



S Cl

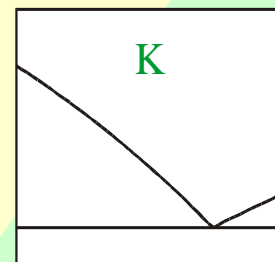
$$\min G(T, p, \{N_k\}) = \sum_p^P \sum_i^C N_i^{(p)} \mu_i^{(p)}$$

1200

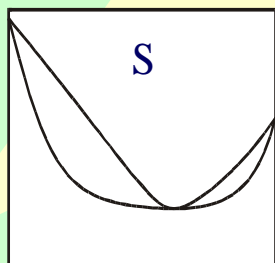


S SO4

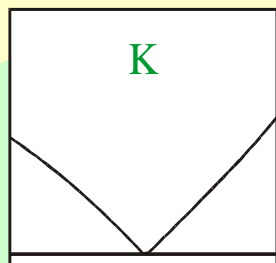
600



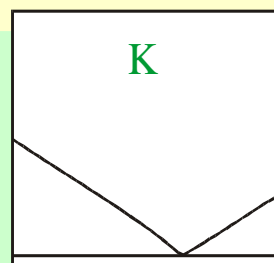
SO4 Cl



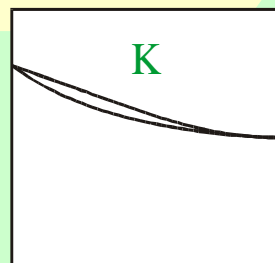
Na K



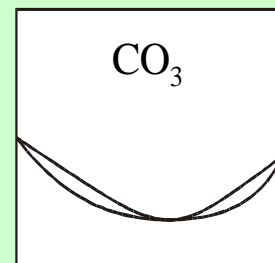
S CO3



CO3 Cl



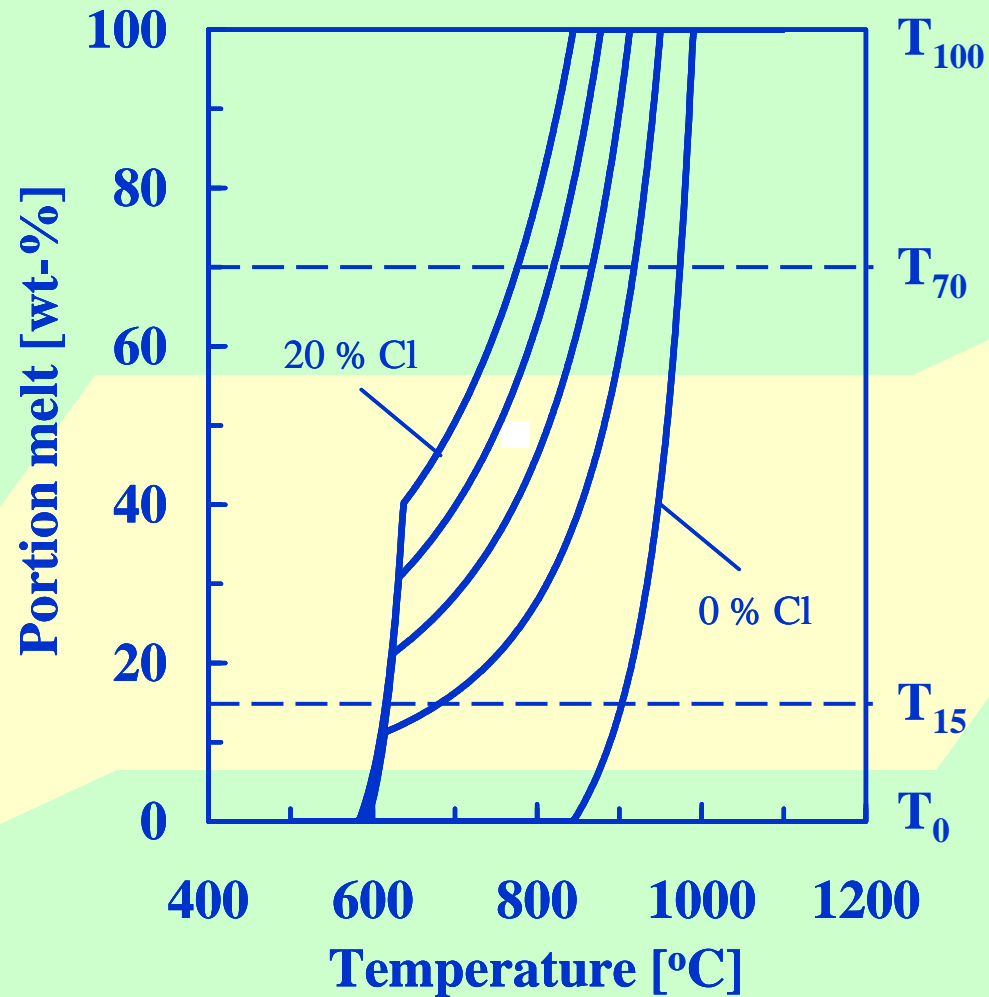
SO4 CO3



K Na

Melting curves for alkali ash

K/Na = 90/10, SO₄/CO₃ = 80/20

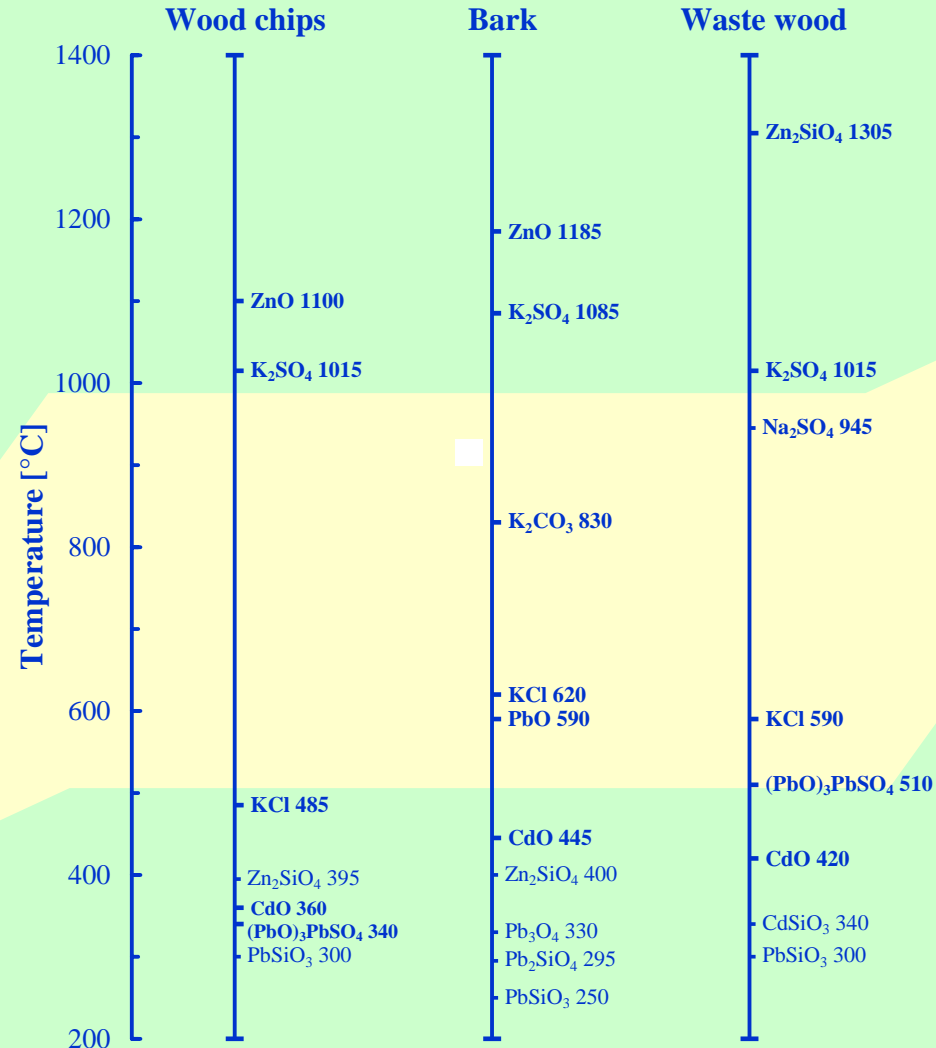


ESTIMATION OF COMPOSITION

- **Prediction based on fuel composition**
- **Aerosol formation models**
- **Condensation chemistry**
 - **Influence of total alkali**
 - **Influence of Na, Cl, S**

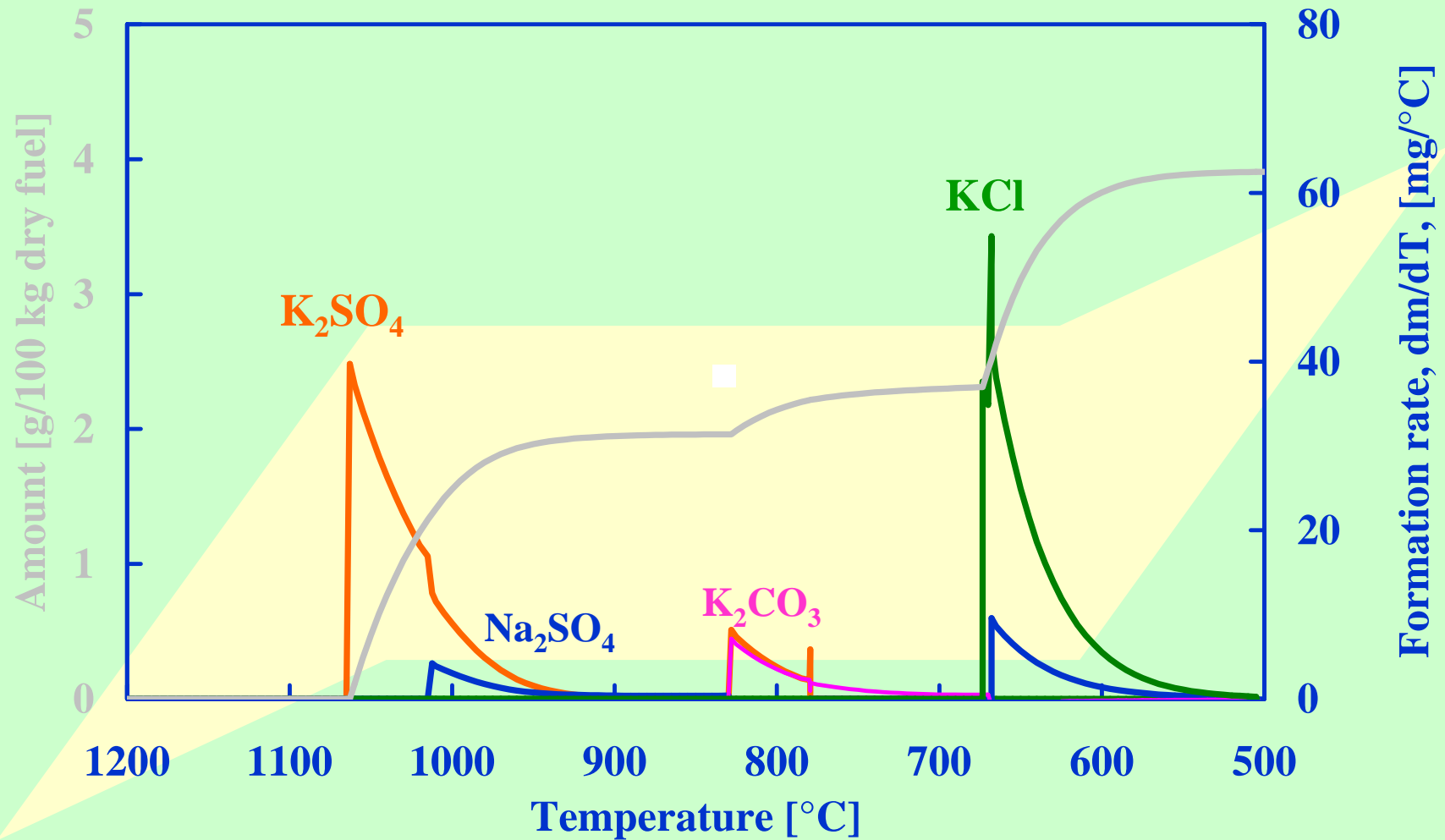
Condensation sequences at cooling

O₂ = 6 % in flue gases



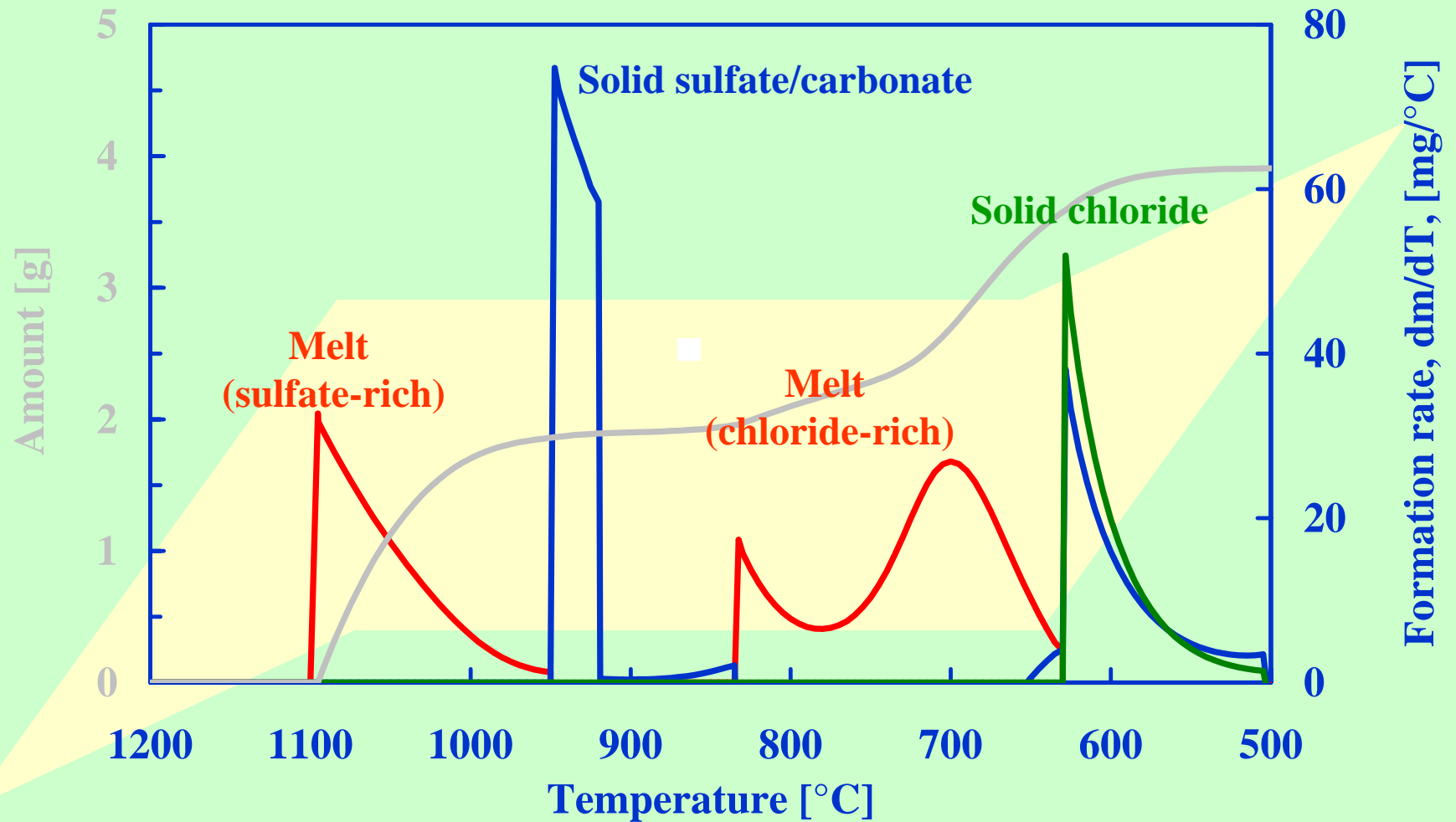
Alkali condensation – pure compounds

$\text{Na}/(\text{K}+\text{Na}) = 0.2$, $\text{Cl}/(\text{K}+\text{Na}) = 0.45$, $\text{S}/(\text{K}_2+\text{Na}_2) = 0.45$



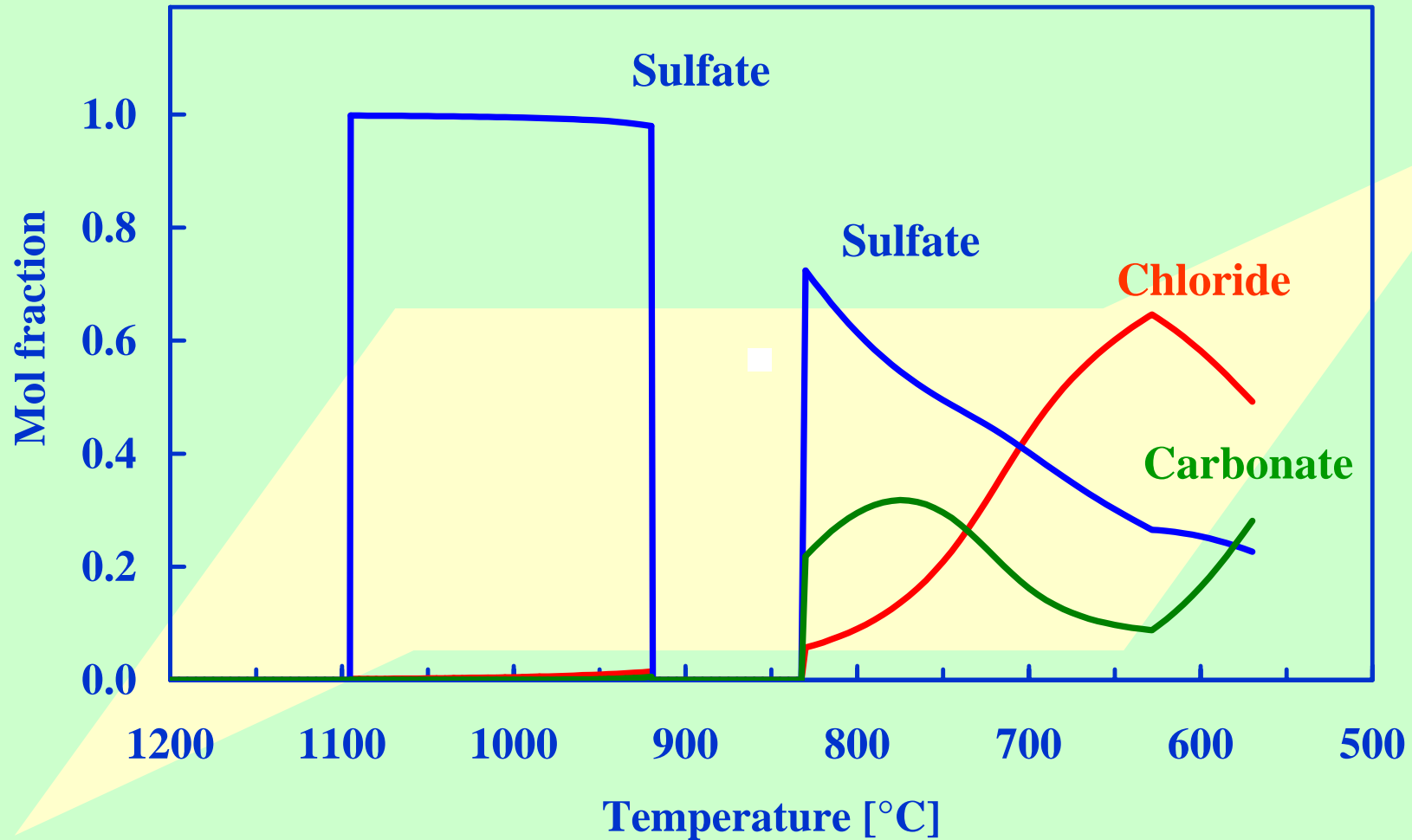
Alkali condensation – melt formation

$\text{Na}/(\text{K}+\text{Na}) = 0.2$, $\text{Cl}/(\text{K}+\text{Na}) = 0.45$, $\text{S}/(\text{K}_2+\text{Na}_2) = 0.45$



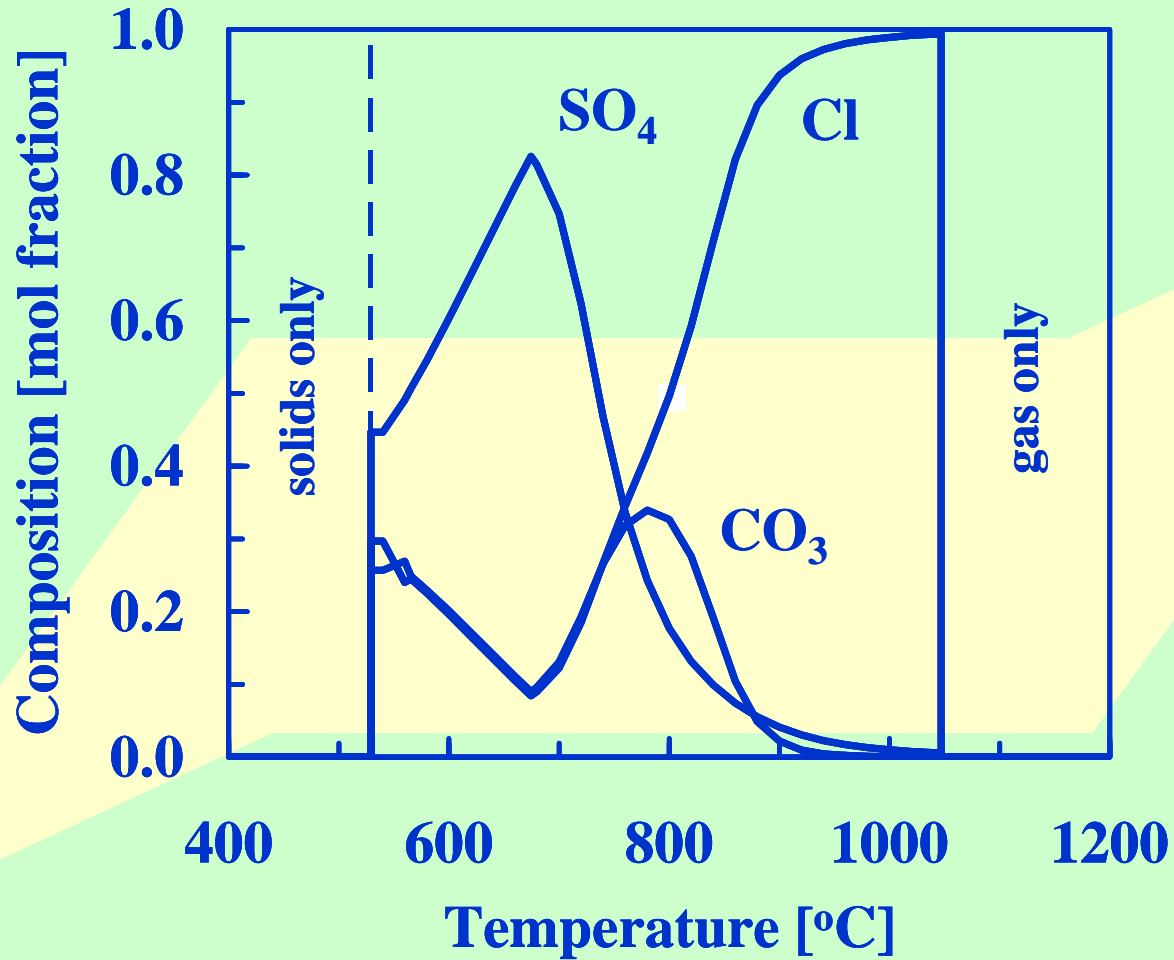
Alkali condensation – melt composition

$\text{Na}/(\text{K}+\text{Na}) = 0.2$, $\text{Cl}/(\text{K}+\text{Na}) = 0.45$, $\text{S}/(\text{K}_2+\text{Na}_2) = 0.45$



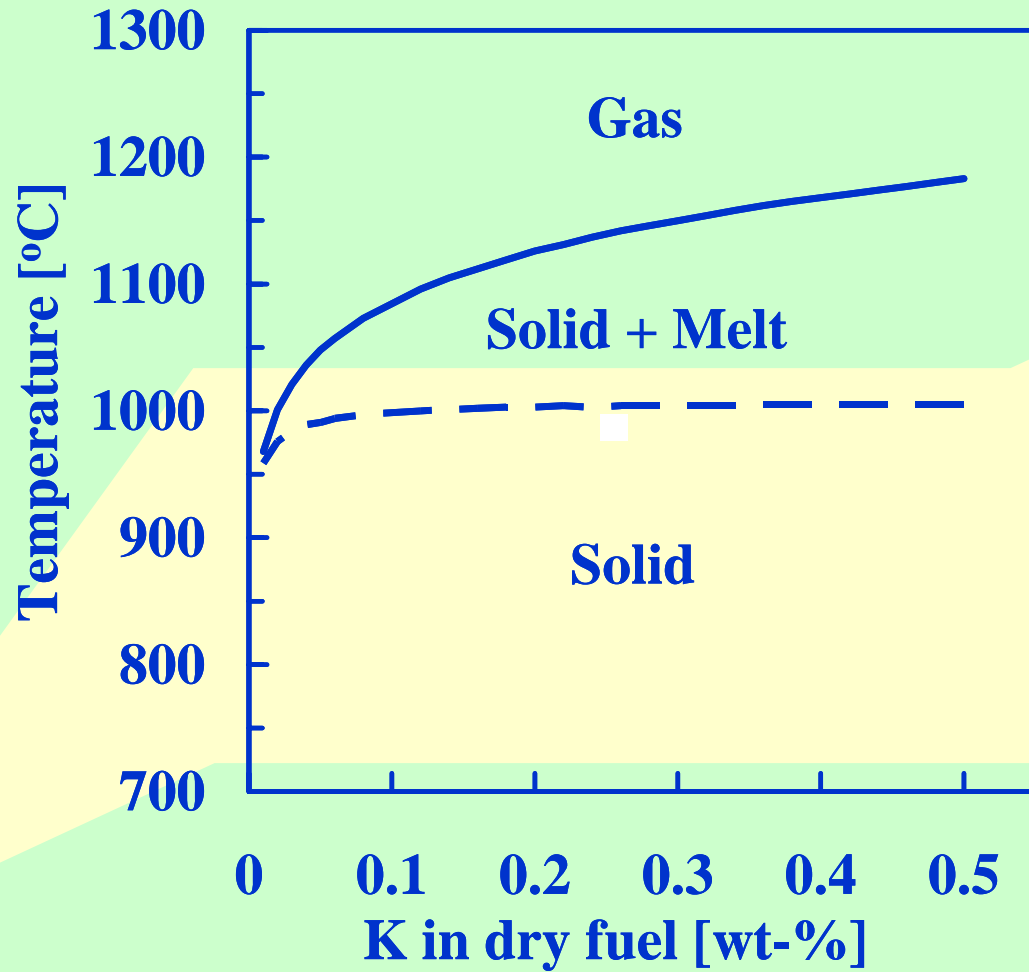
Melt composition

$\text{Na}/(\text{K}+\text{Na}) = 0.2$, $\text{Cl}/(\text{K}+\text{Na}) = 0.8$, $\text{S}/(\text{K}_2+\text{Na}_2) = 0.1$



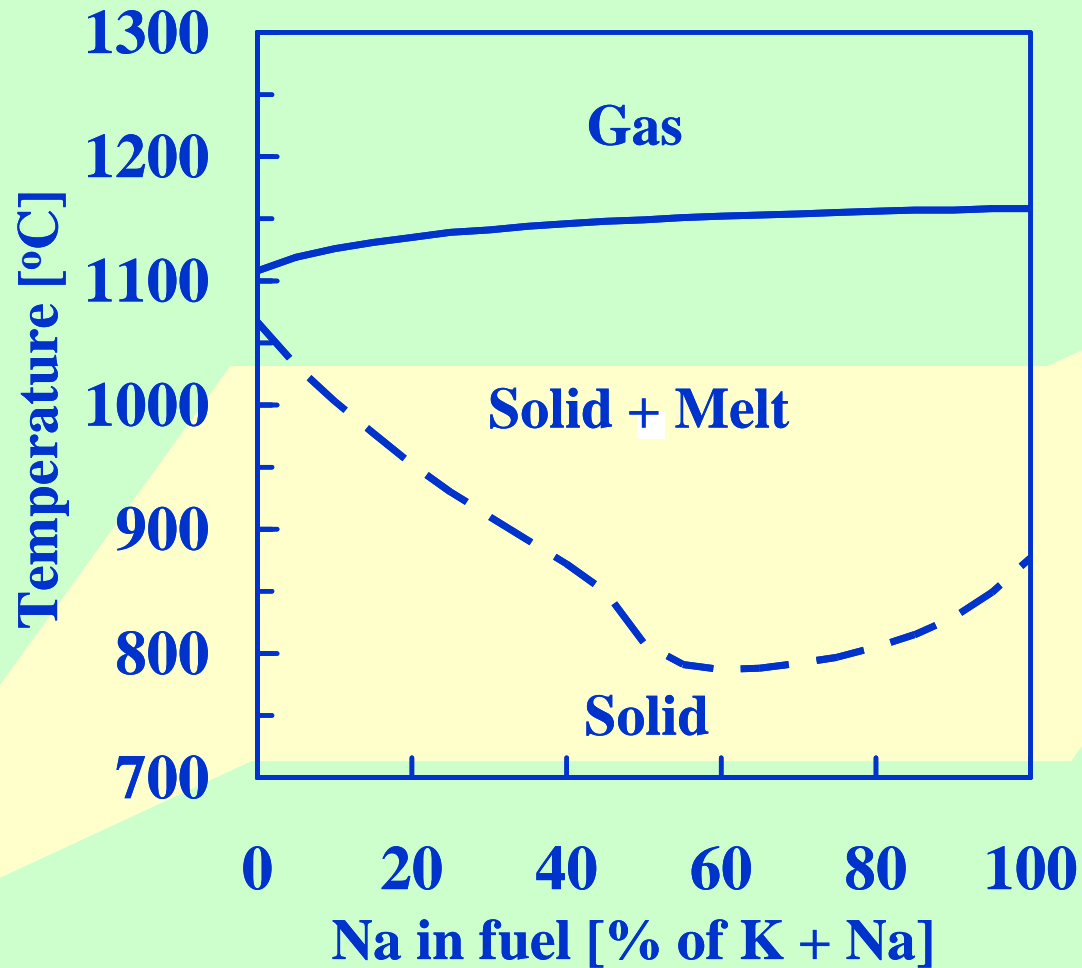
Influence of potassium

$\text{Na}/(\text{K}+\text{Na}) = 0.1$, $\text{Cl}/(\text{K}+\text{Na}) = 0.05$, $\text{S}/(\text{K}_2+\text{Na}_2) = 0.95$



Influence of sodium

K in dry fuel = 0.2 %, Cl/(K+Na) = 0.05, S/(K₂+Na₂) = 0.95

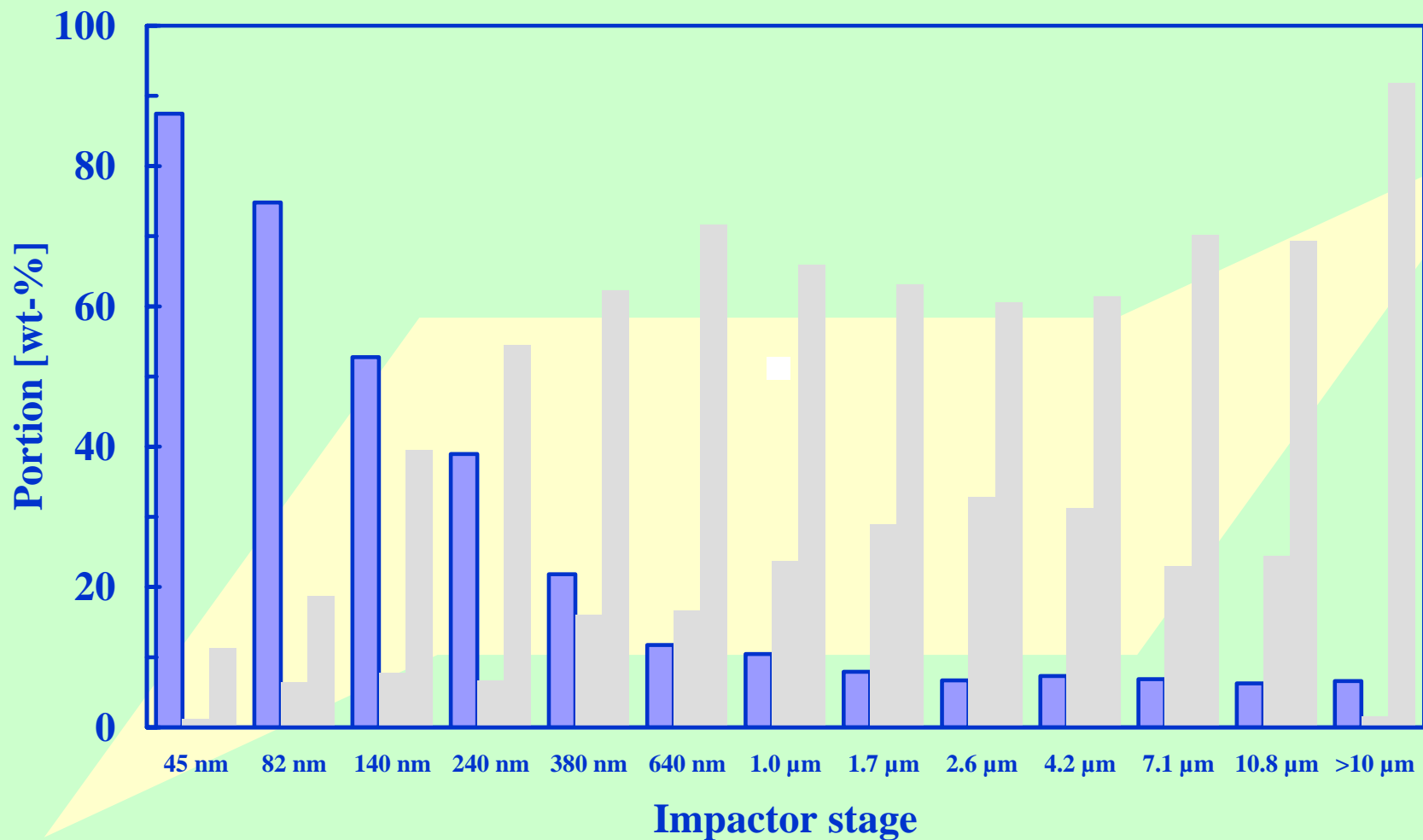


MELTING OF ASH FRACTIONS

- **Impactor measurements**
 - **Biomass fired BFBC (105 MW)**
 - **Chemical composition by SEM/EDX**
 - **Al, Ca, Fe, K, Mg, Mn, Na, Si, Ti, Cl, S, P**
 - **Estimation of speciation (compounds)**
 - **Calculated melting curves**
- **Coarse ash fraction**
 - **Biomass grate firing**

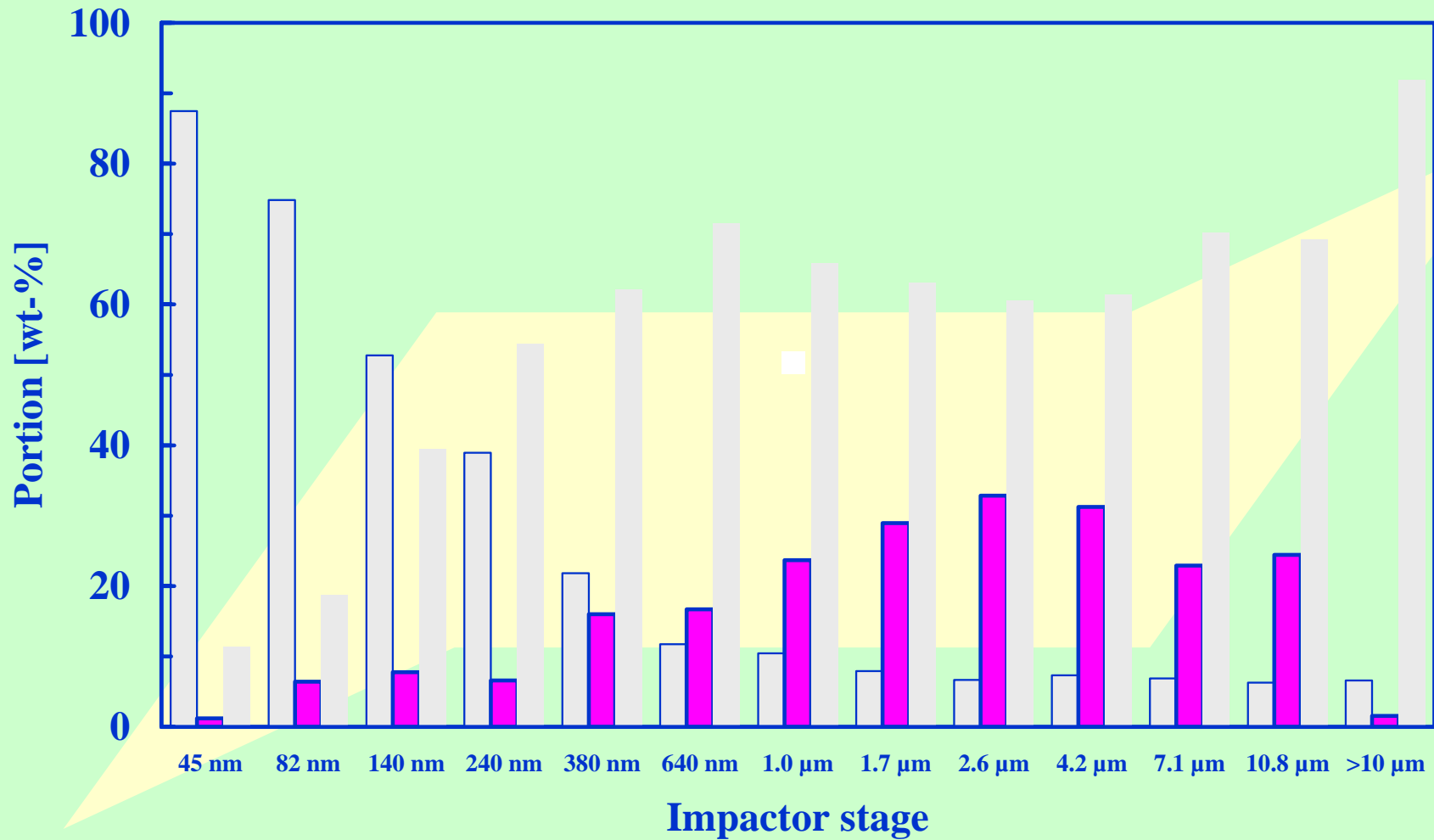
Alkali part (K, Na) of fine particles

Biomass combustion, BFBC



Calcium salt part (SO_4 , CO_3) of fine particles

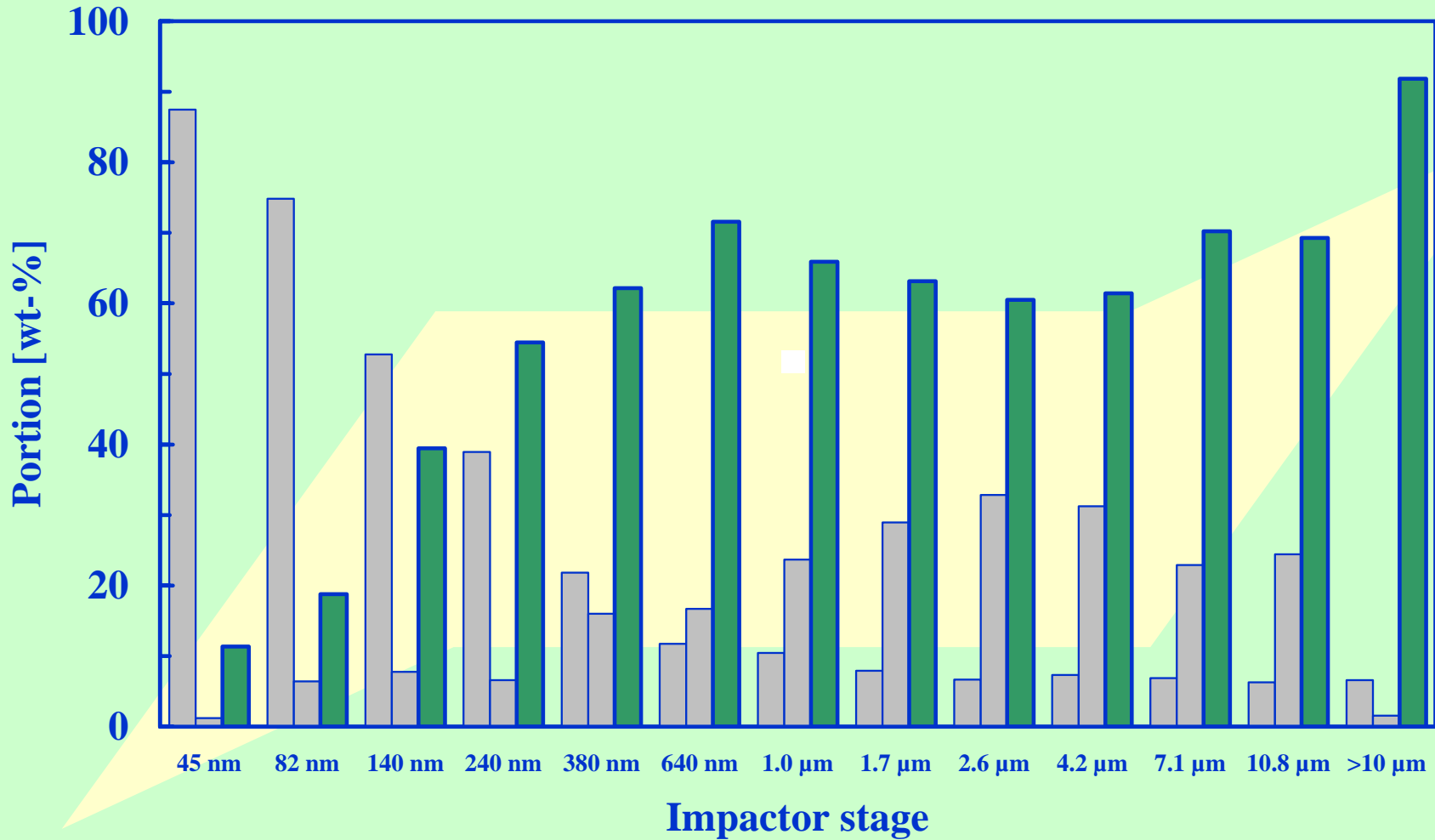
Biomass combustion, BFBC



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Inert part (oxides silicates) of fine particles

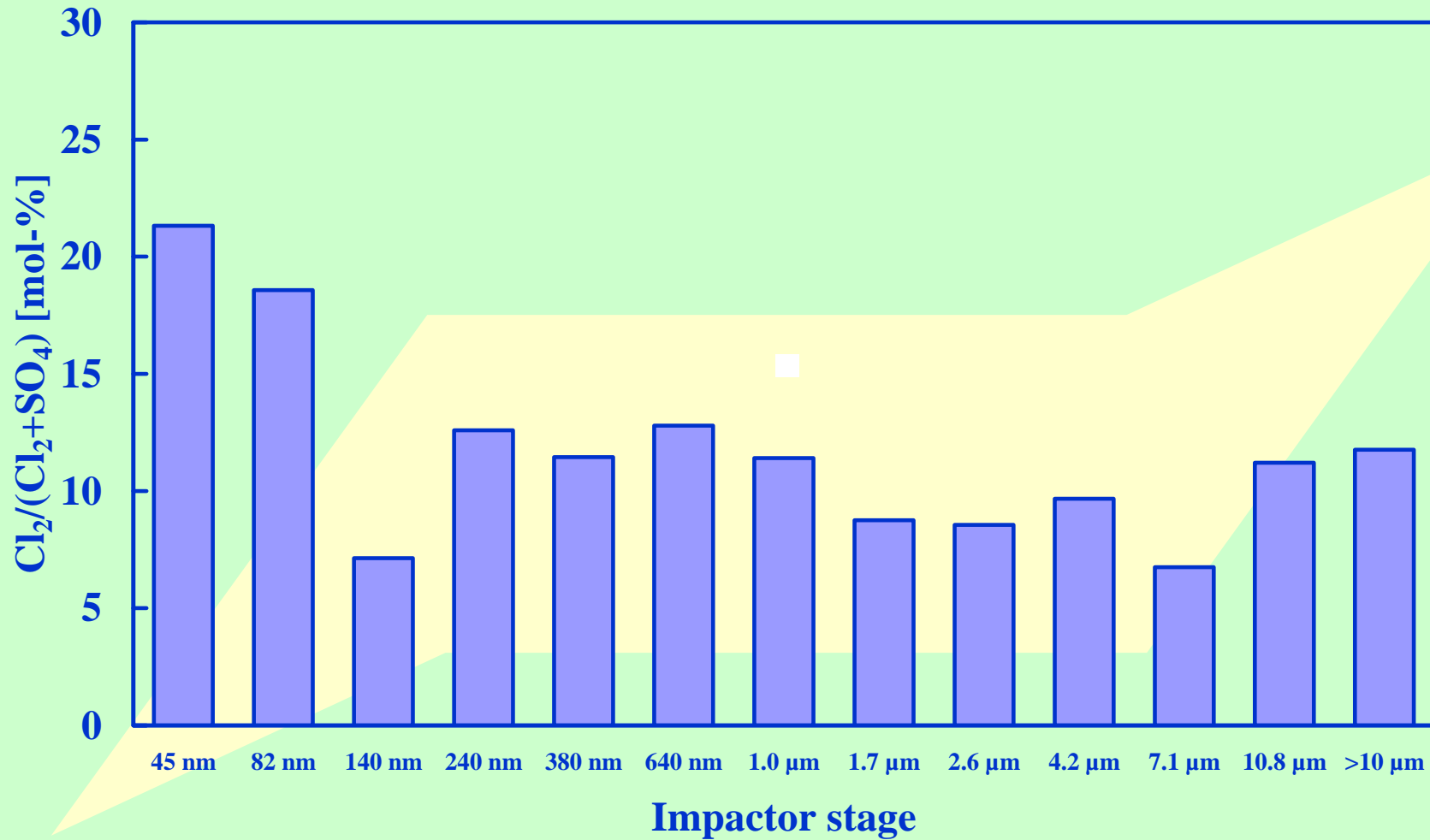
Biomass combustion, BFBC



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Chloride and sulfate of fine particles

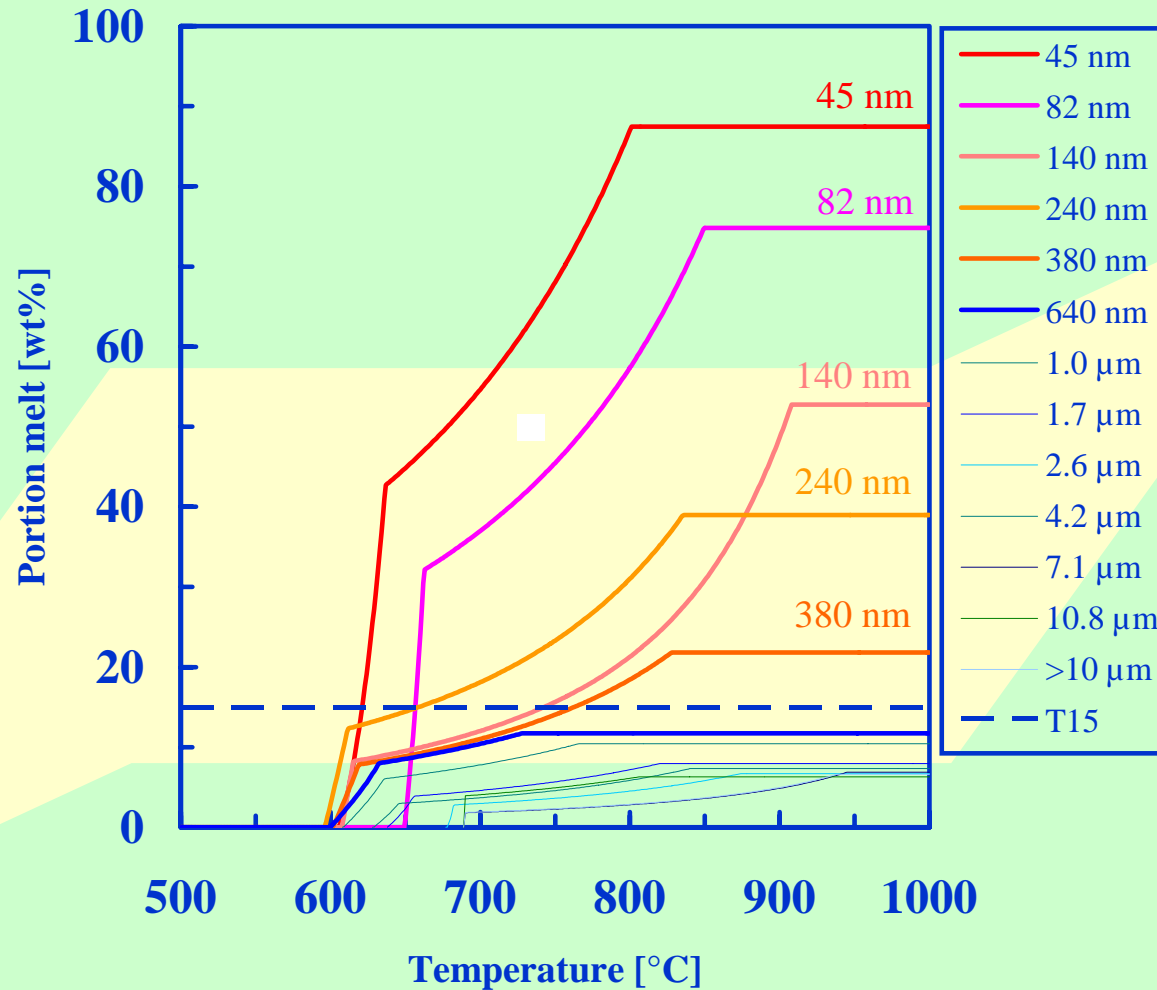
Biomass combustion, BFBC



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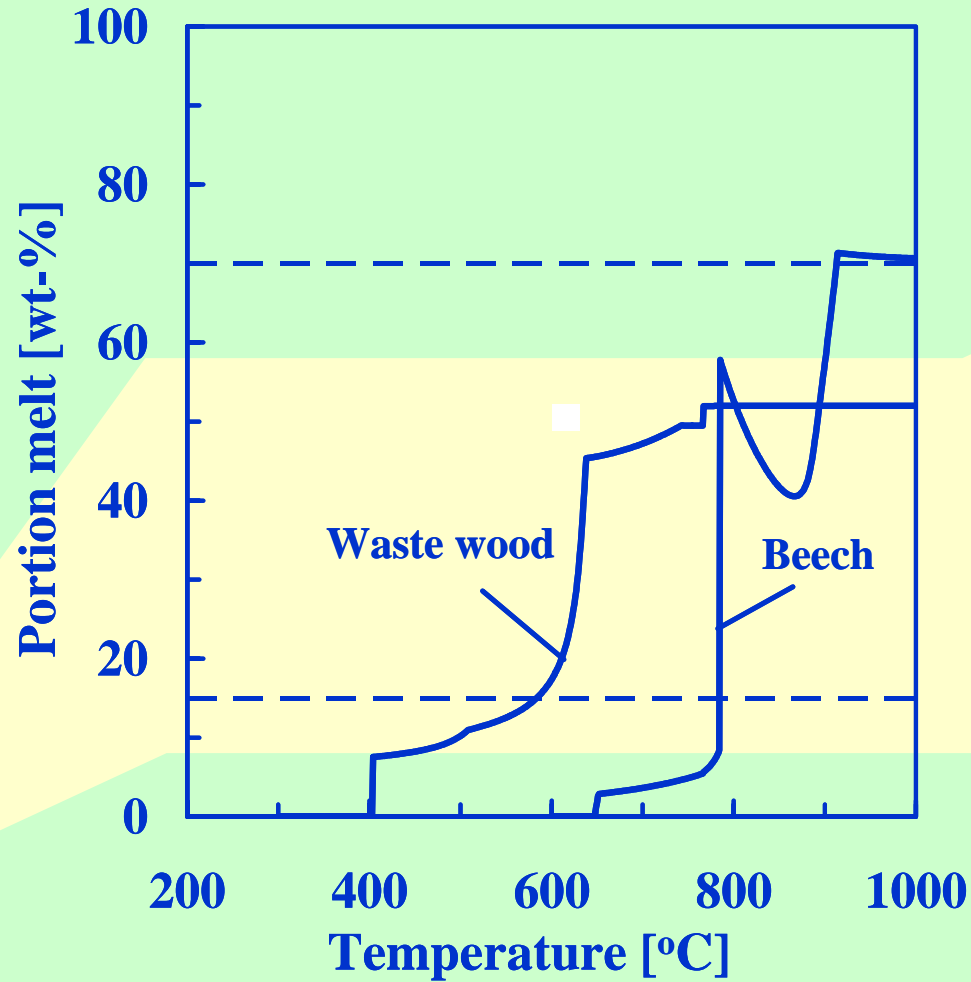
Melting curves of impactor samples

Biomass combustion, BFBC



Melting curves of coarse ash

Grate biomass firing

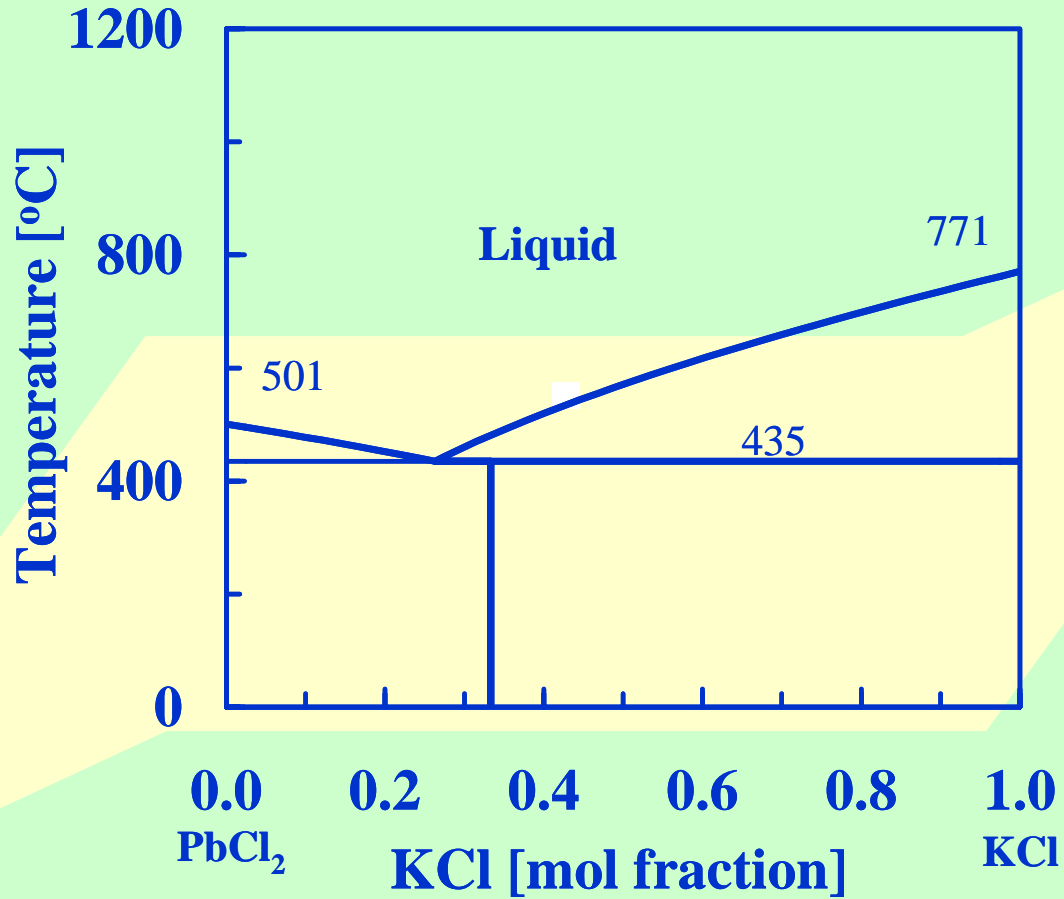


INFLUENCE OF LEAD AND ZINC

- **Alkali chlorides + Pb and Zn**
- **Biomass grate firing**
- **Calculated cases**

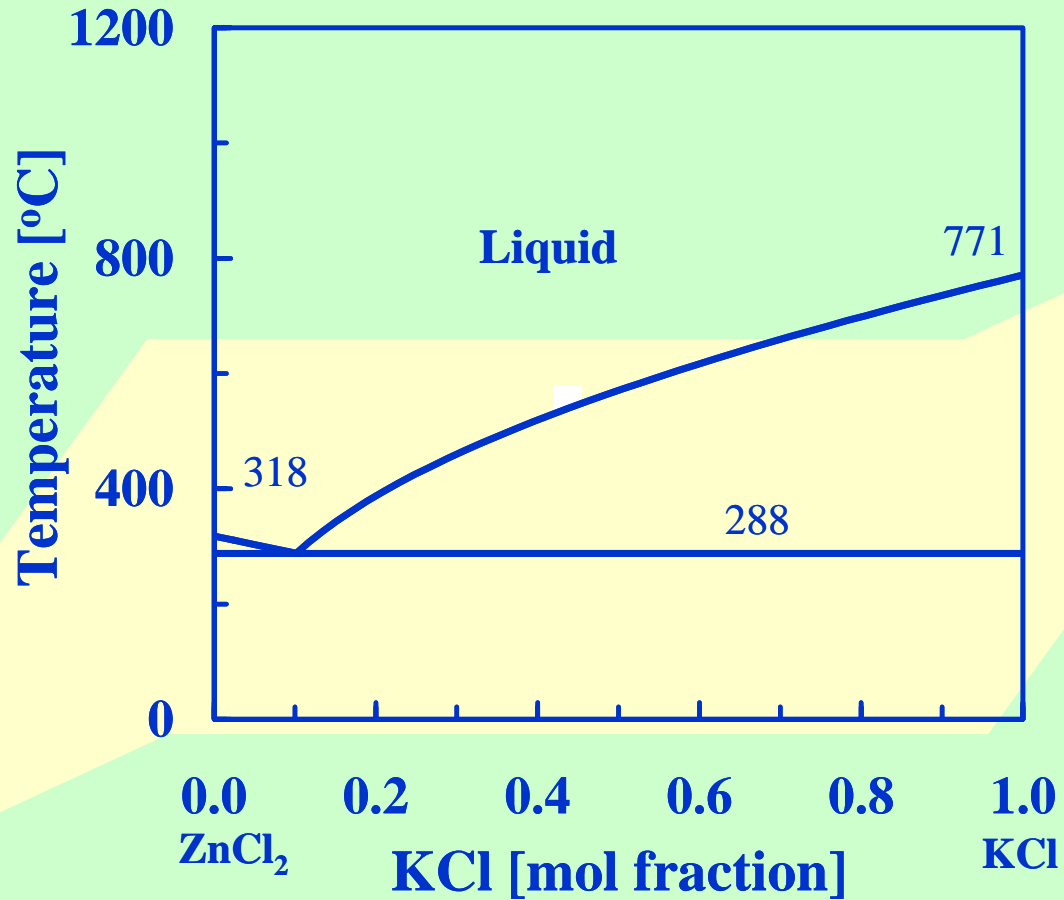
Calculated phase diagram KCl-PbCl₂

ÅAU-model

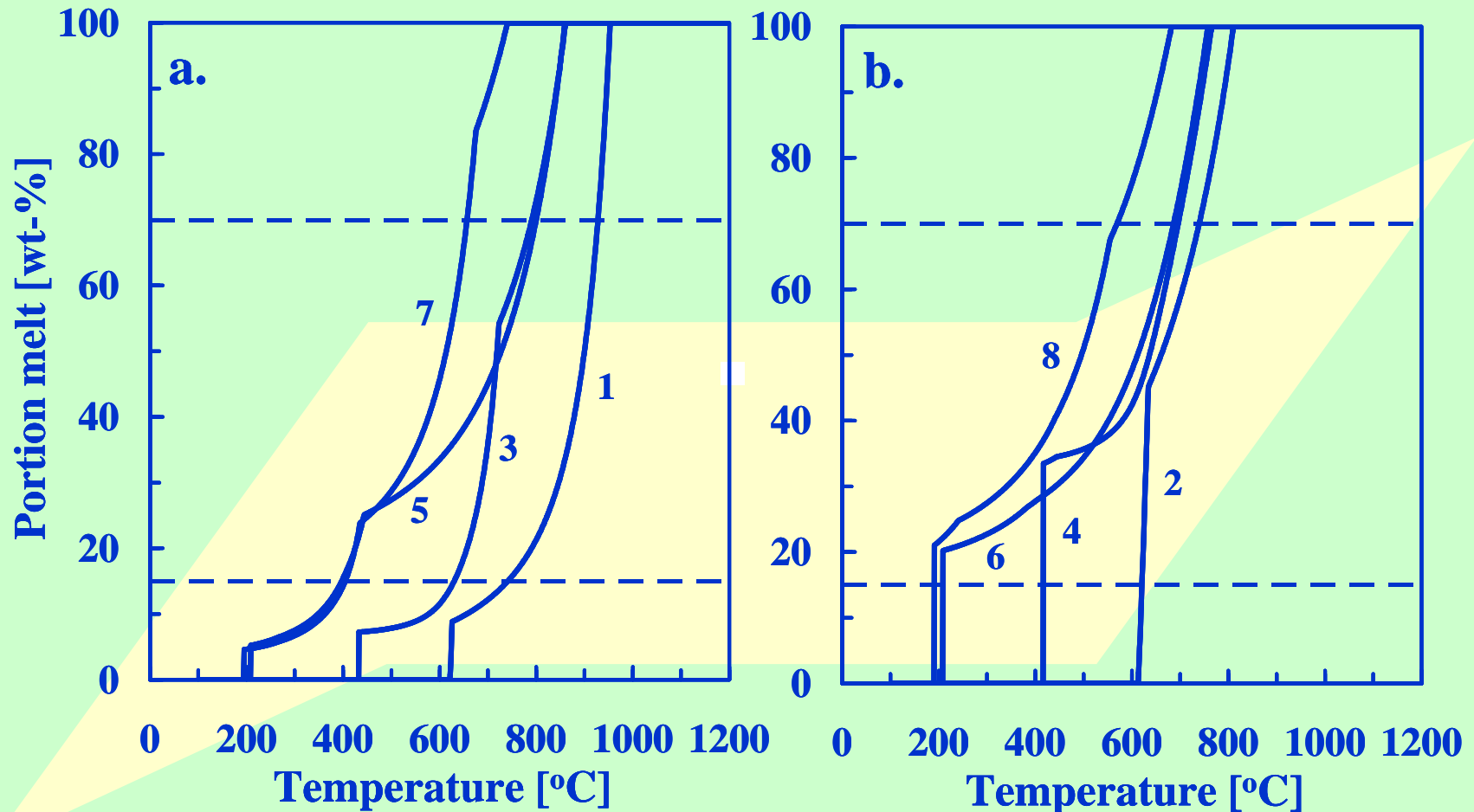


Calculated phase diagram KCl-ZnCl₂

ÅAU-model



Calculated melting curves for condensing fume with Pb and Zn. a) low Cl, b) high Cl



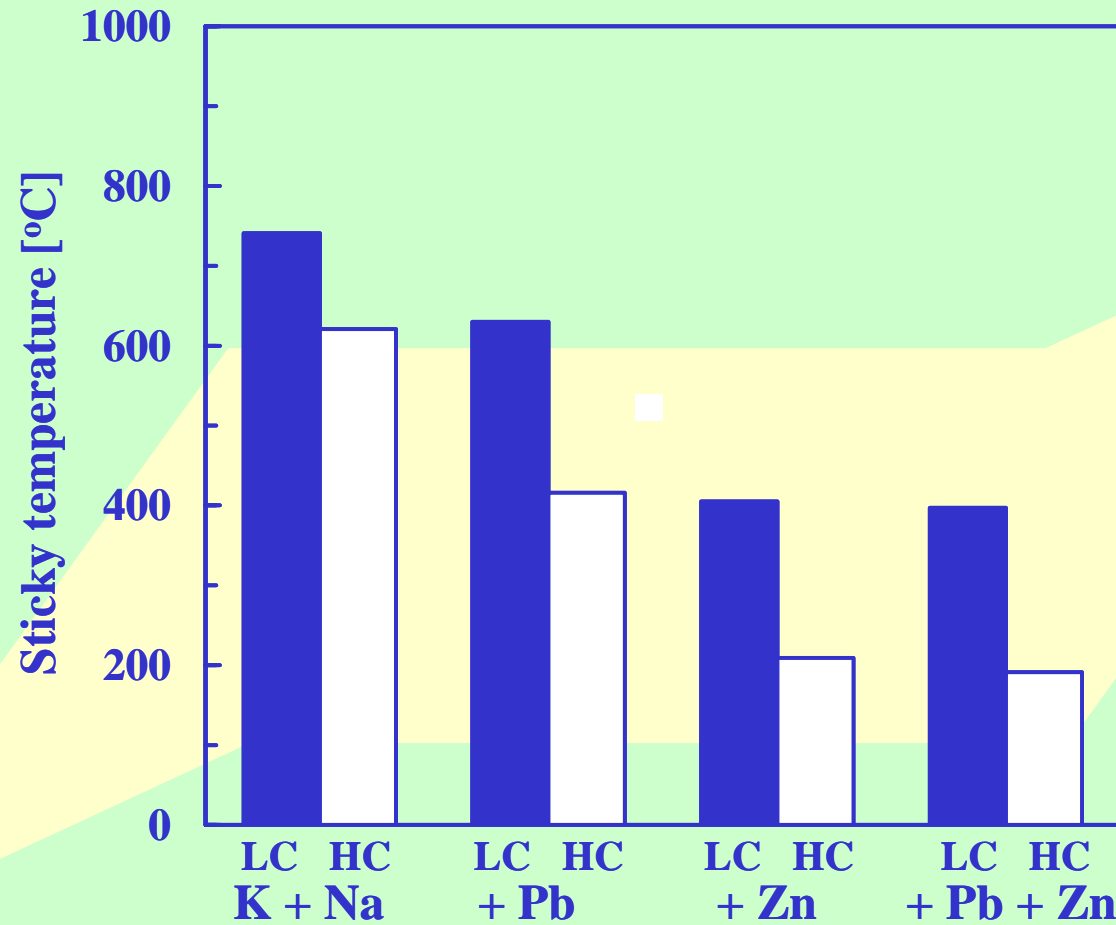
Calculated cases for condensing fume with Pb and Zn

Case #	Cl ₂ /A ^(*) m/m	Na ₂ /A m/m	Pb/A m/m	Zn/A m/m
1	5	20	0	0
2	25	20	0	0
3	5	20	20	0
4	25	20	20	0
5	5	20	0	20
6	25	20	0	20
7	5	20	20	20
8	25	20	20	20

*) A = K₂ + Na₂ + Pb + Zn = Cl₂ + SO₄ mol

Sticky temperature dependency of Pb and Zn

LC: low chloride, HC: high chloride



CONCLUSIONS

- Melting properties of ash fractions affect deposit formation and growth
- Melting properties can be estimated if chemical composition is known
- Composition can be estimated based on thermodynamic considerations
- Stickiness strongly dependent of composition
- Ratio Cl/S critical for alkali fume melting $\rightarrow T_0 \approx 550^\circ\text{C}$
- Presence of lead and zinc in alkali fume can decrease T_0 to 200°C

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