PROCESS CHEMISTRY CENTRE

ÅBO AKADEMI UNIVERSITY

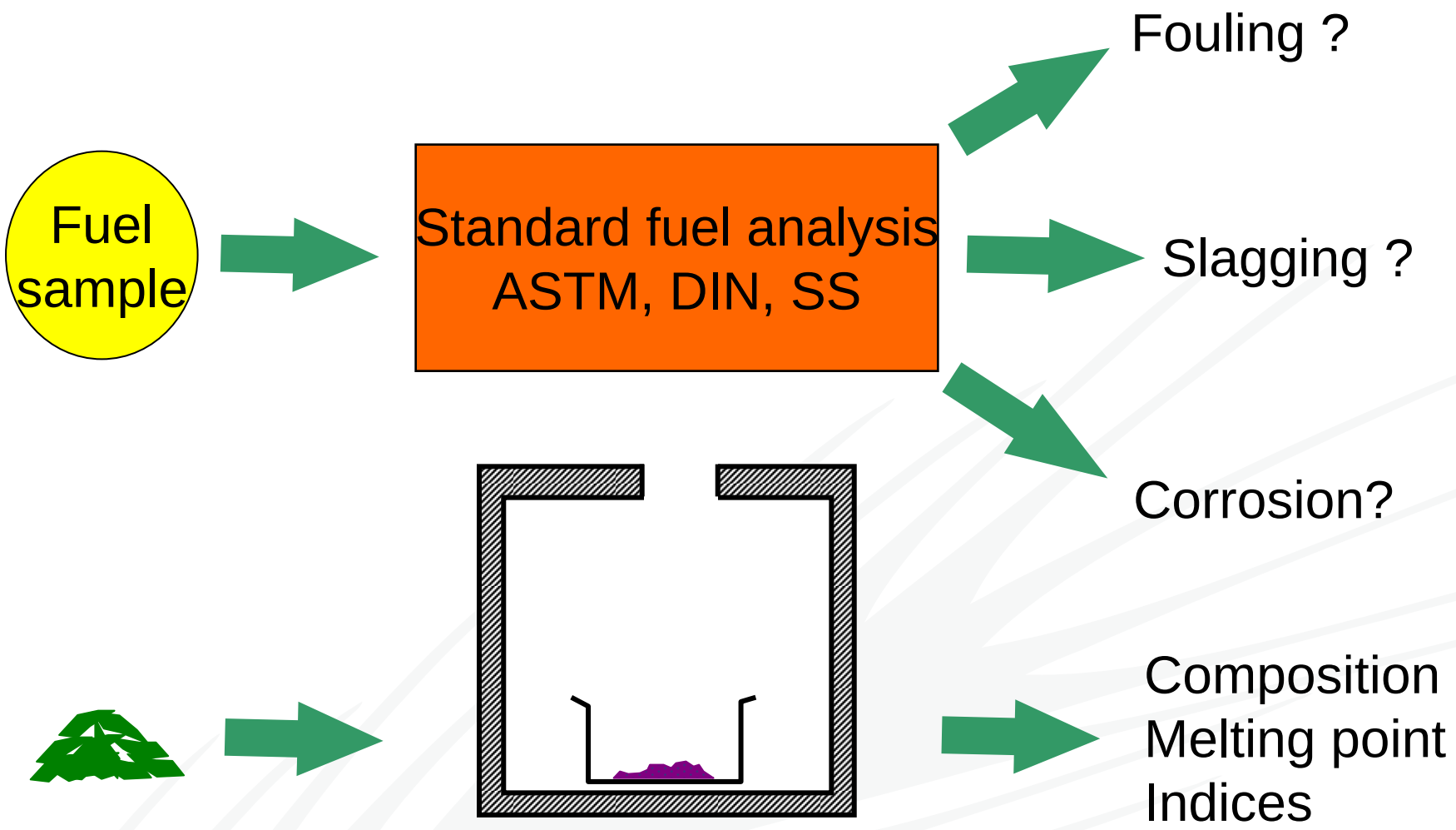
Ash chemistry
Why doing fuel analyses?

Maria Zevenhoven, Patrik Yrjas,
Bengt-Johan Skrifvars,
Mikko Hupa

Topics

- Standard laboratory ash
- Ash forming matter – advanced analysis
- Fly ash composition
- Ash melting
- Co-firing

Standard Ash Analysis



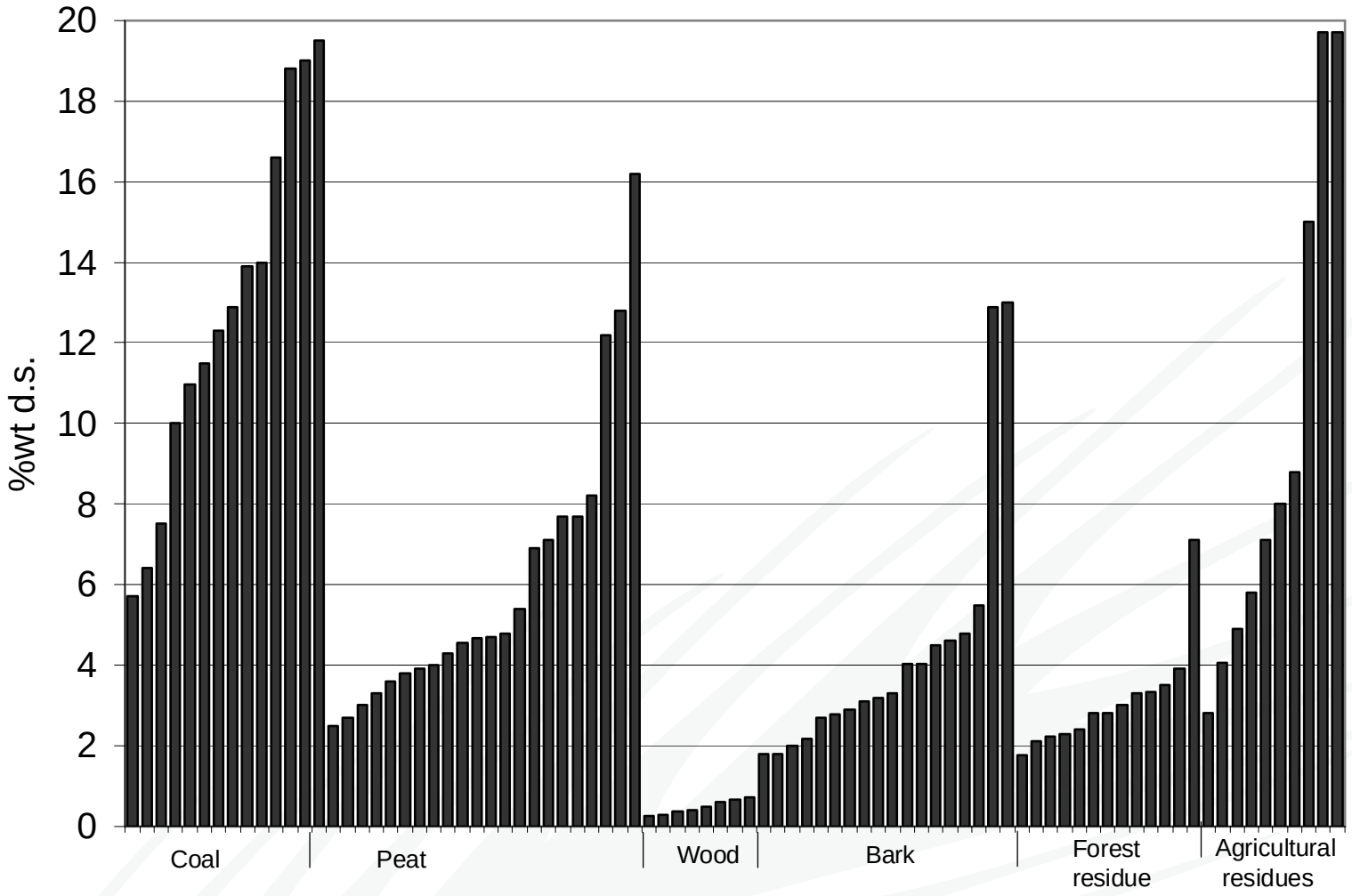
Fly Ash Deposit vs. Laboratory Ash for Biomass Fuels

- Higher alkali
- Higher chloride
- Possible reactions with SO_2

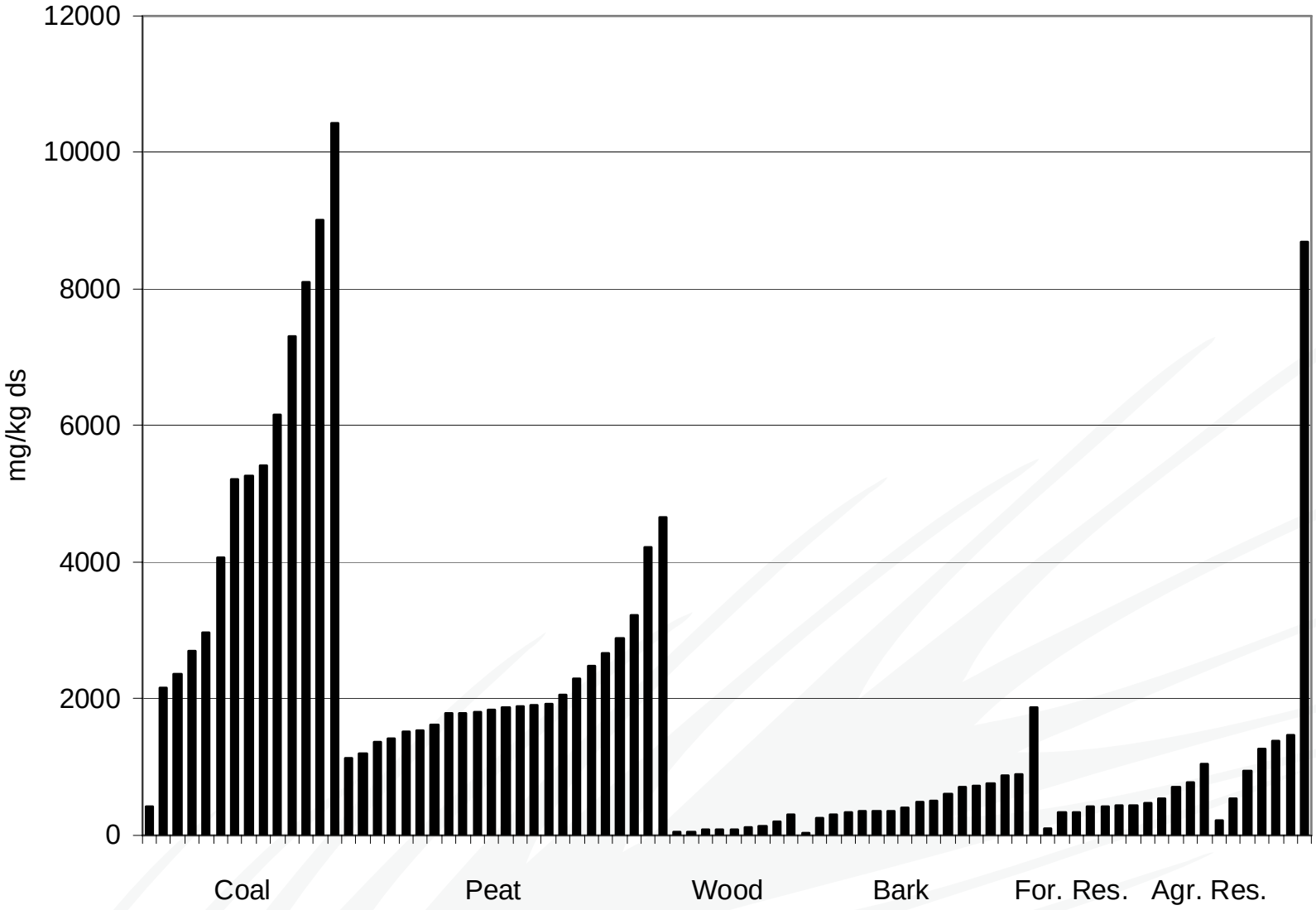
-> Much lower melting range

Fuel characterisation

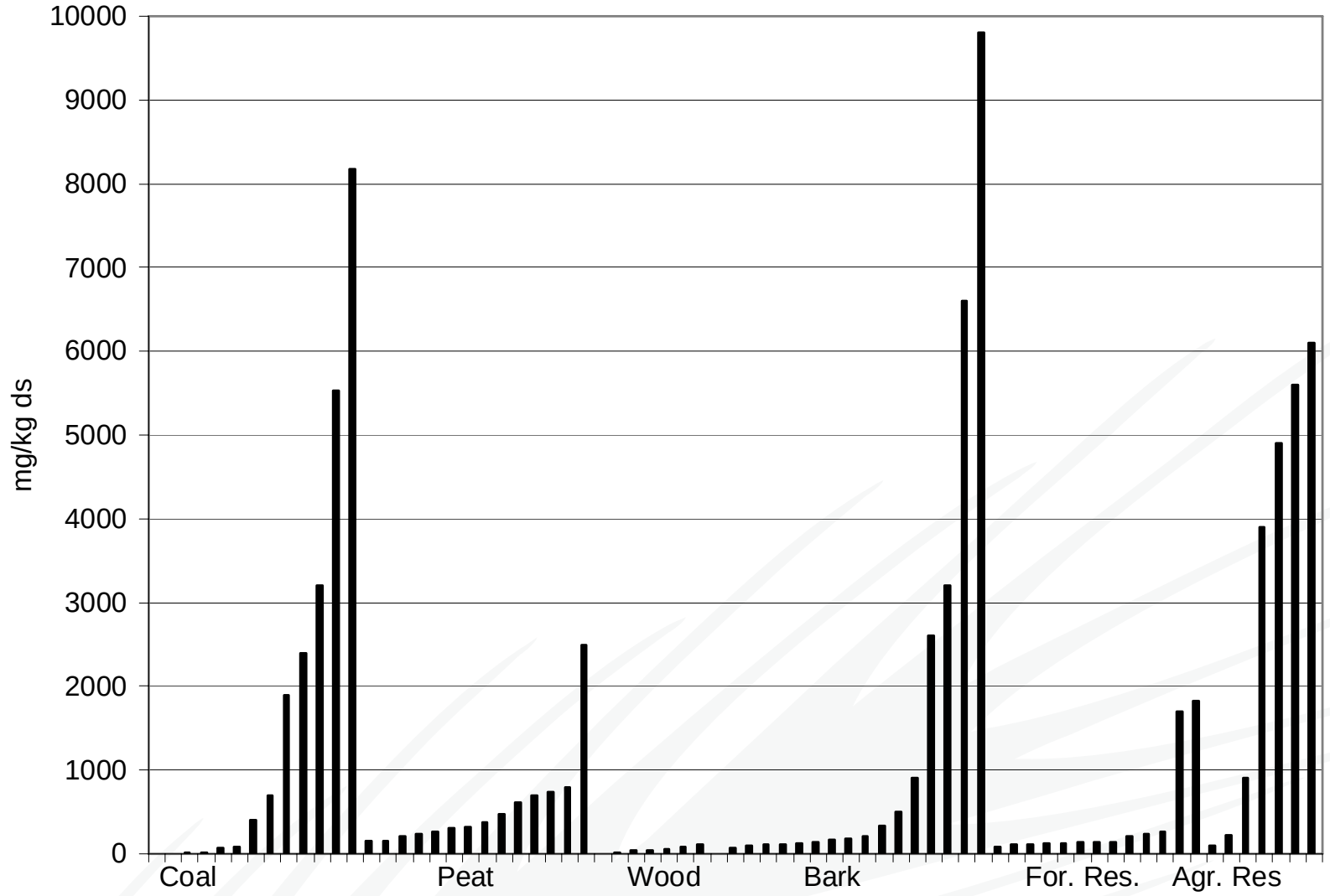
- *Ash content in different fuels*



Total S

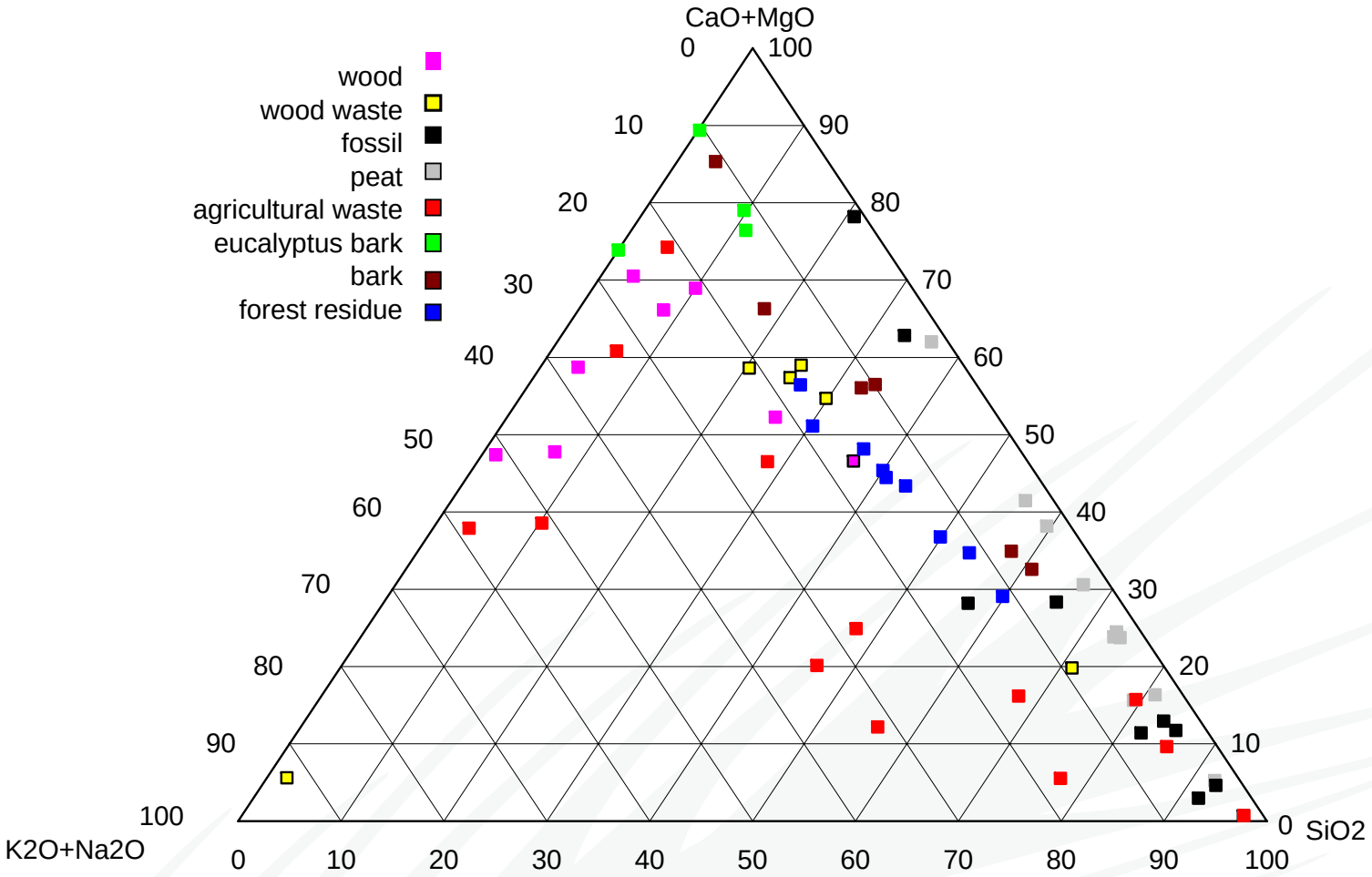

12000
10000
8000
6000
4000
2000
0
mg/kg ds
Coal
Peat
Wood
Bark
For. Res.
Agr. Res.

Total Cl

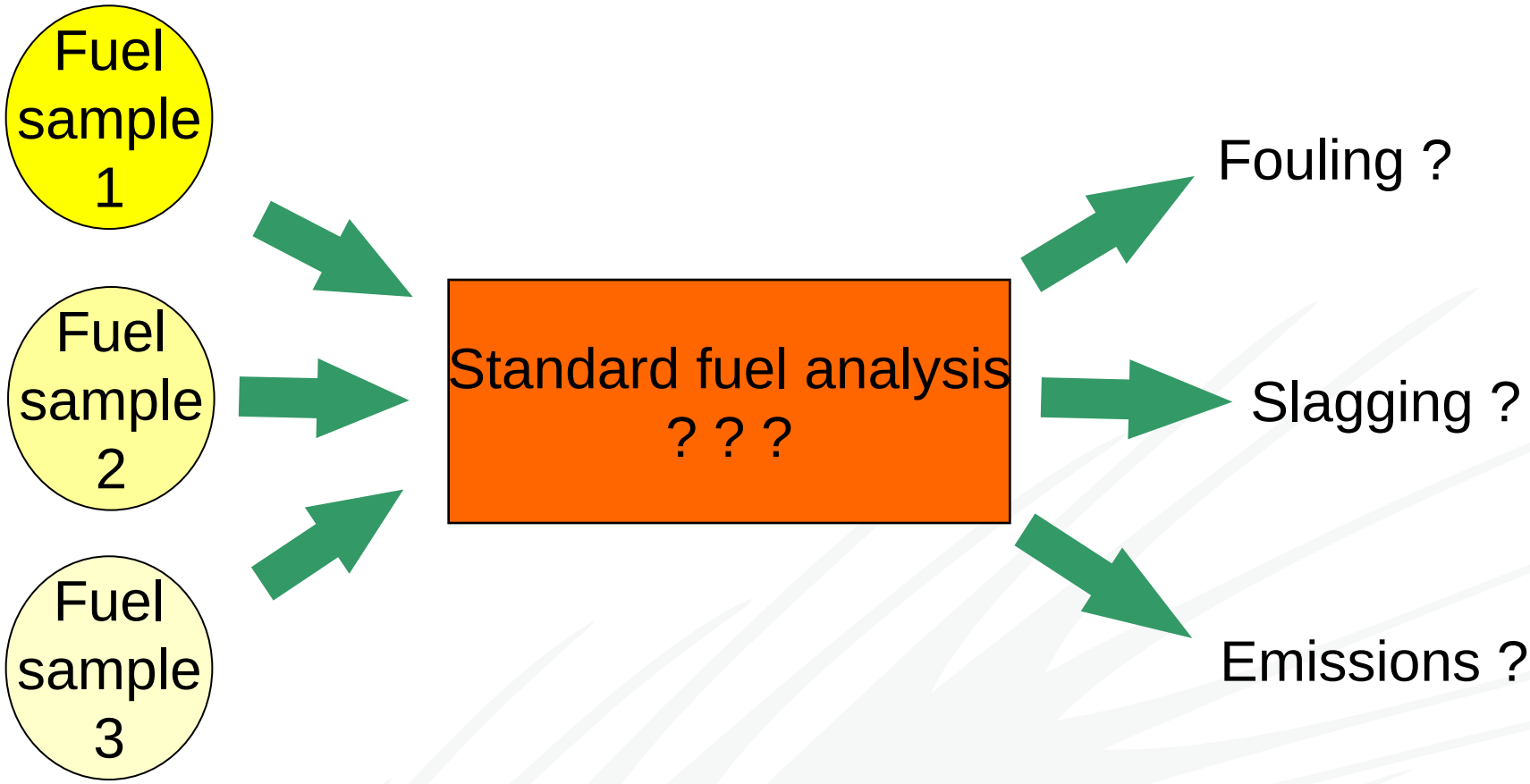

10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
mg/kg ds
Coal
Peat
Wood
Bark
For. Res.
Agr. Res

Analysis of ash forming matter in fuels

- *Triangular composition diagram of ash forming matter*



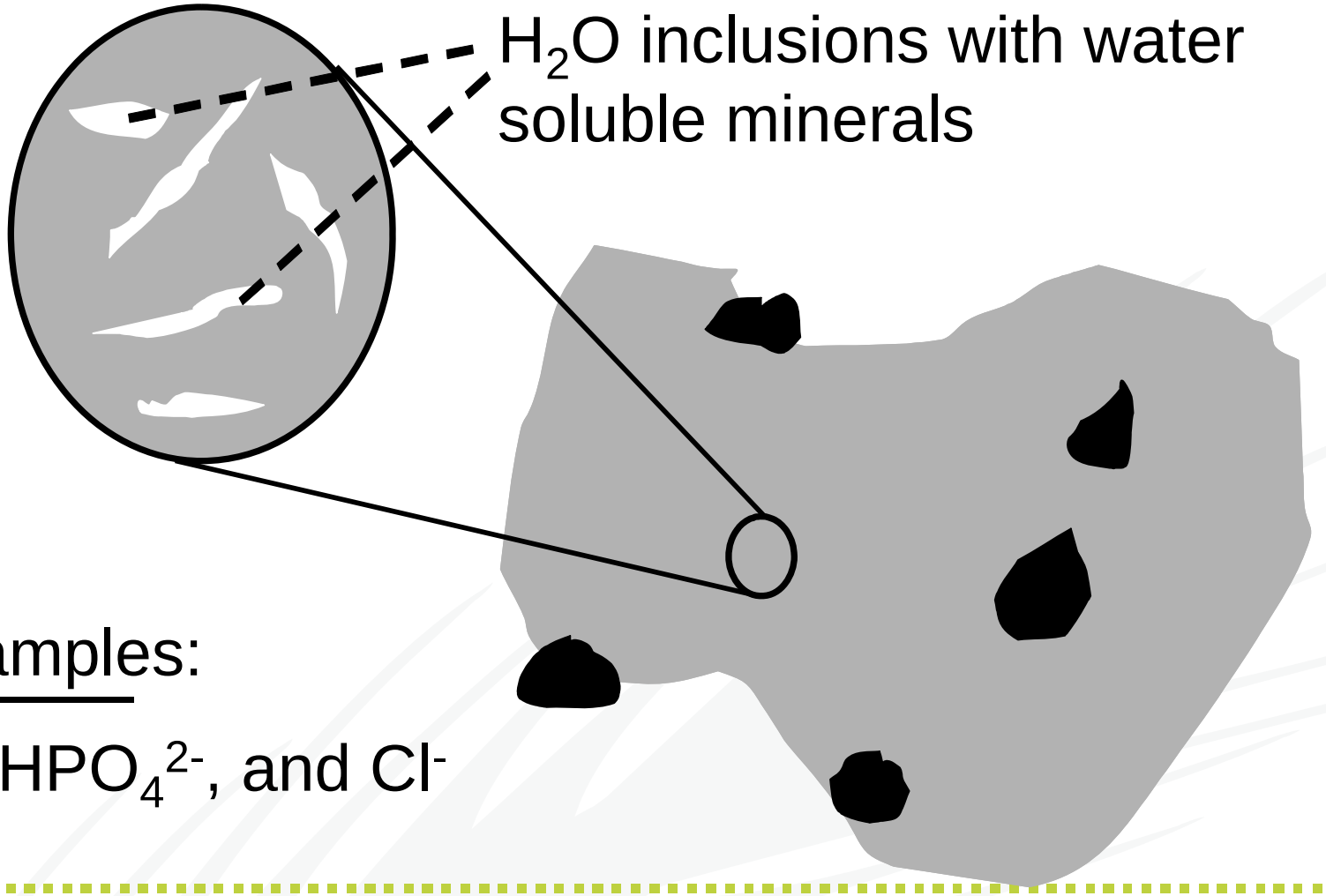
How to Deal with Fuel Mixtures



Topics

- Standard laboratory ash
- Ash forming matter – advanced analysis
- Fly ash composition
- Ash melting
- Co-firing

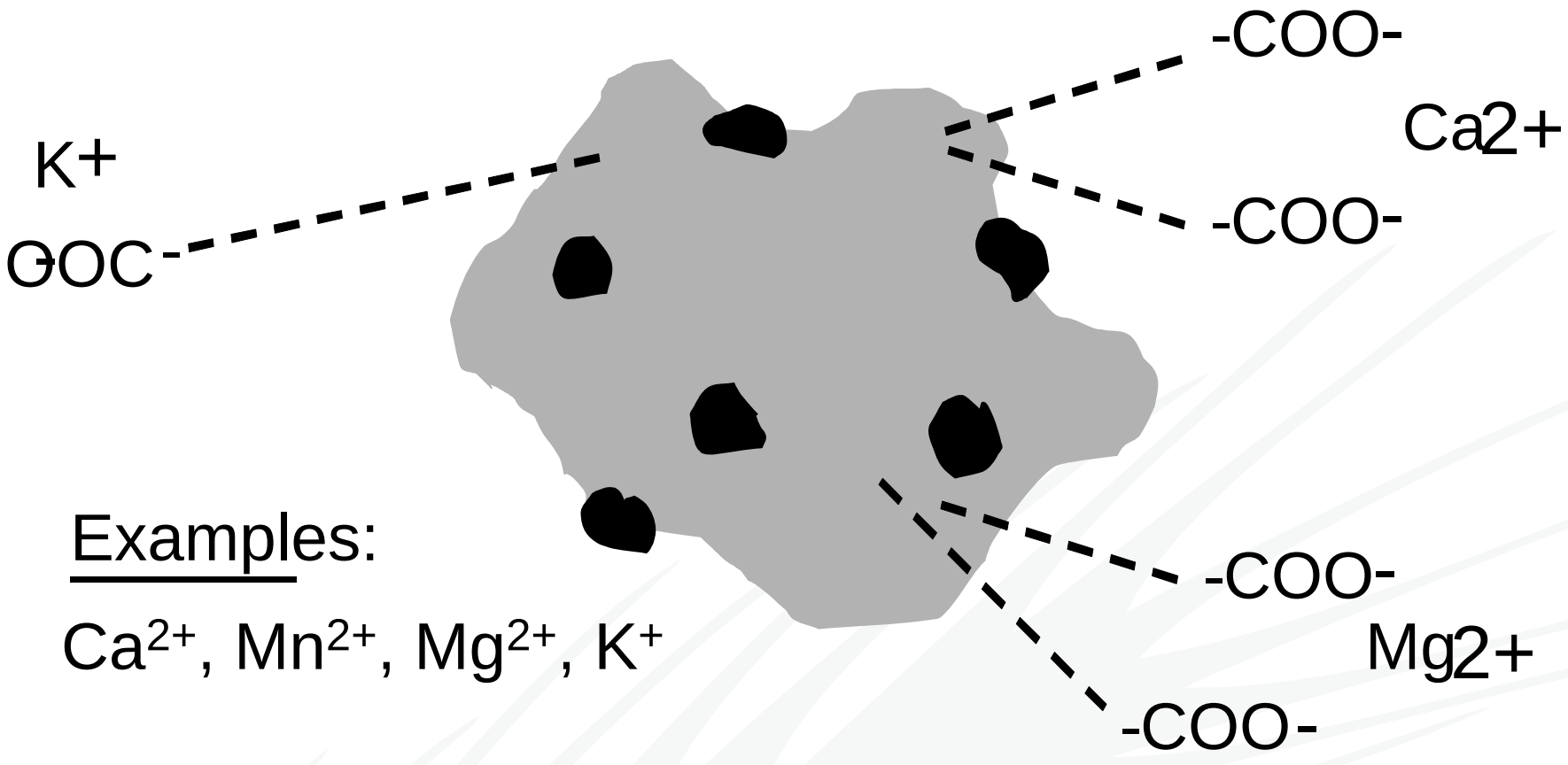
Ash in Biomass Fuels: Ions in Aqueous Solutions



Examples:

K^+, HPO_4^{2-}, and Cl^-

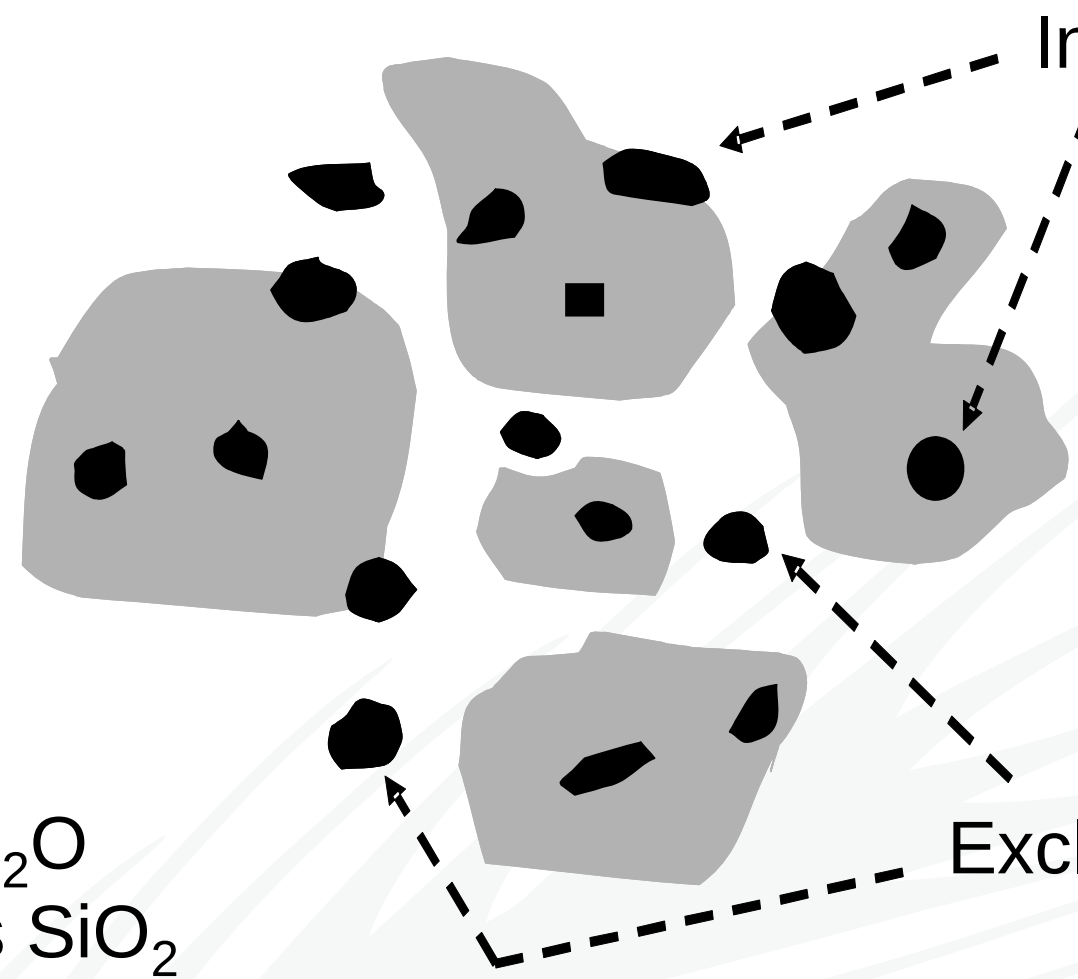
Ash in Biomass Fuels: Organically Associated Metals



Examples:

Ca^{2+}, Mn^{2+}, Mg^{2+}, K^{+}

Ash in Biomass Fuels: Included and Excluded Minerals

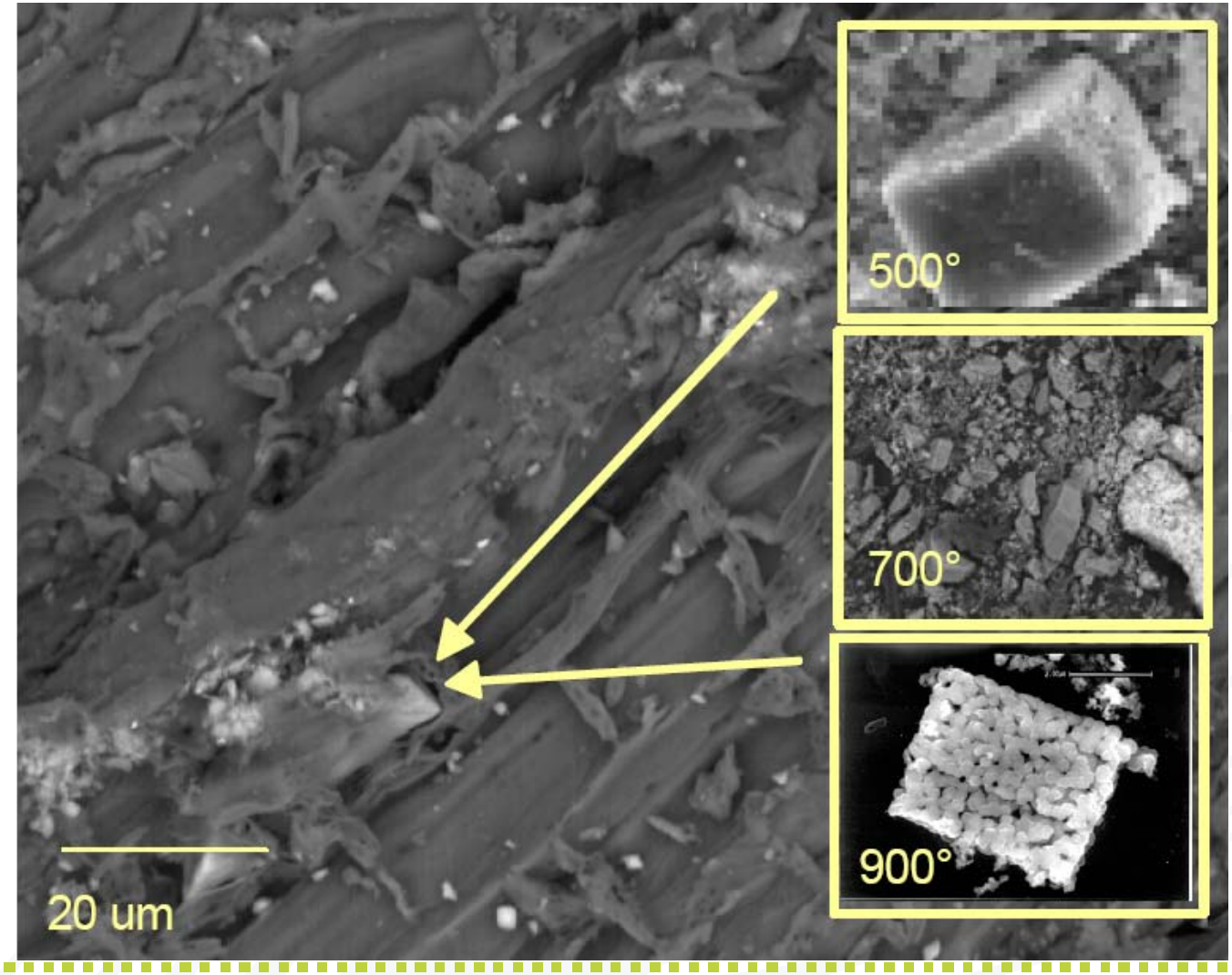


Examples:

$CaC_2O_4 \cdot 2H_2O$

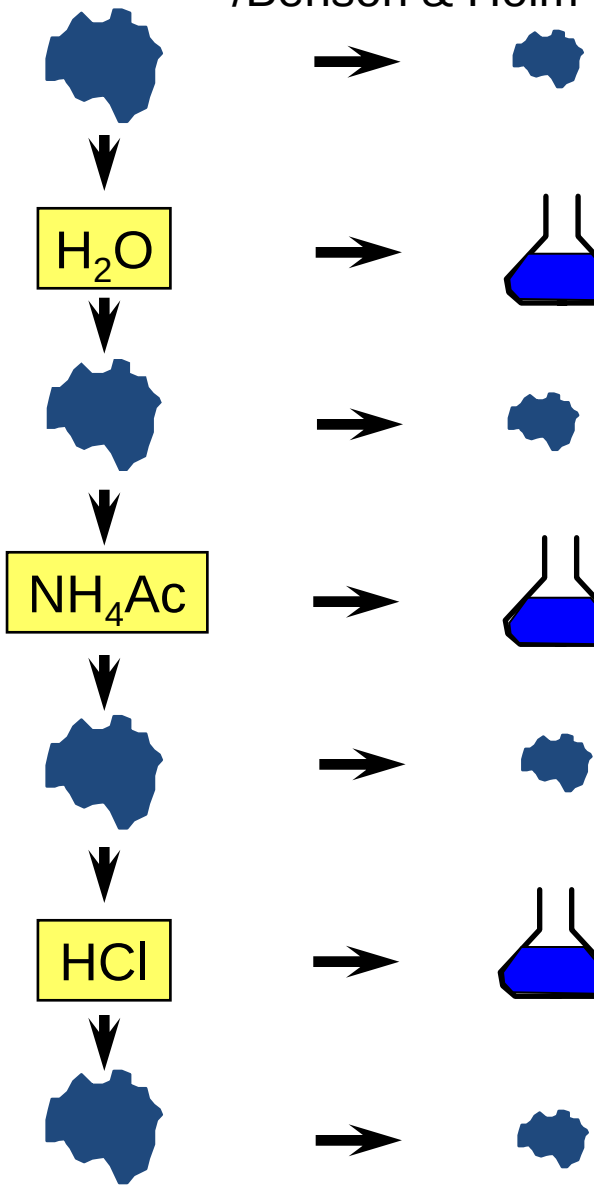
Amorphous SiO_2

SEM Eucalyptus bark



Stepwise leaching

/Benson & Holm 1985, Baxter 1994, Zevenhoven 2001/



Total mineral matter
- all major ash-forming elements

Water leachable
- alkali sulfates/carbonates/chlorides

Buffer solution leachable
- organically associated

Acid leachable
- carbonates/sulfates

Rest
- silicates, unsoluble rest

Stepwise leaching

/Benson & Holm 1985, Baxter 1994, Zevenhoven 2001/

Total mineral matter

All major ash-forming elemen

Easily soluble

Water leachable

-alkali sulfates/carbonates/ chlorides

Buffer solution leachable

- organically associated

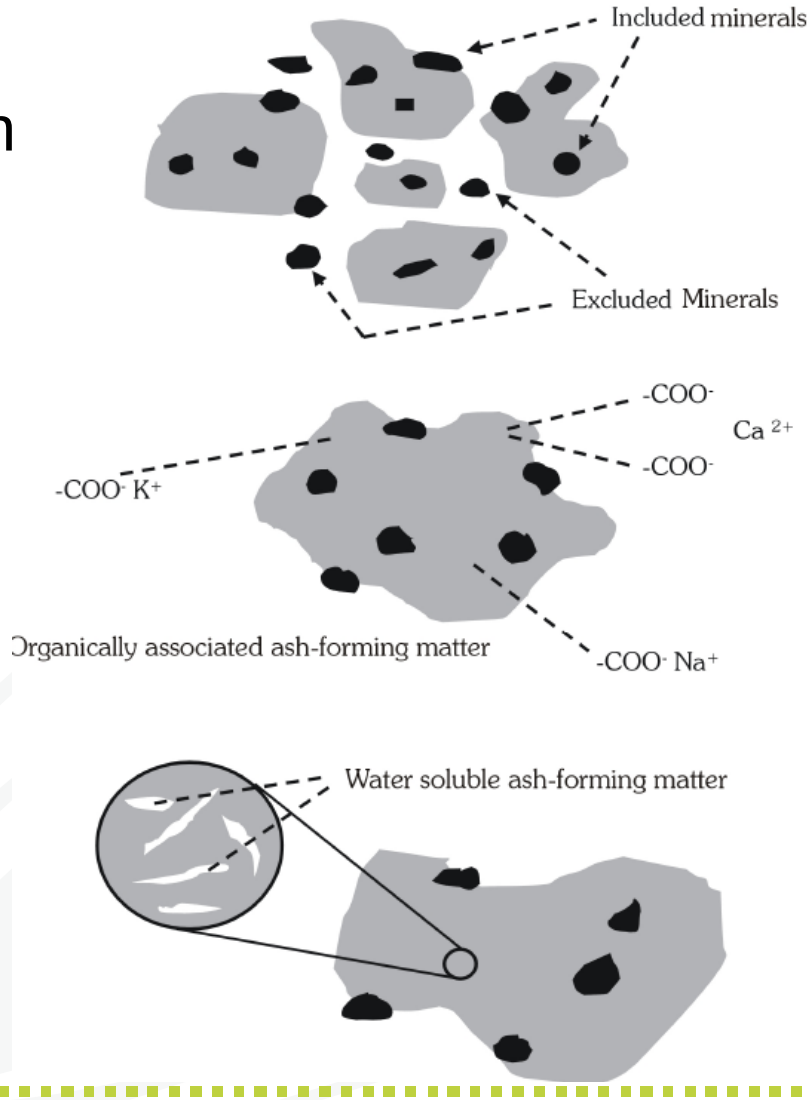
Mineral part

Acid leachable

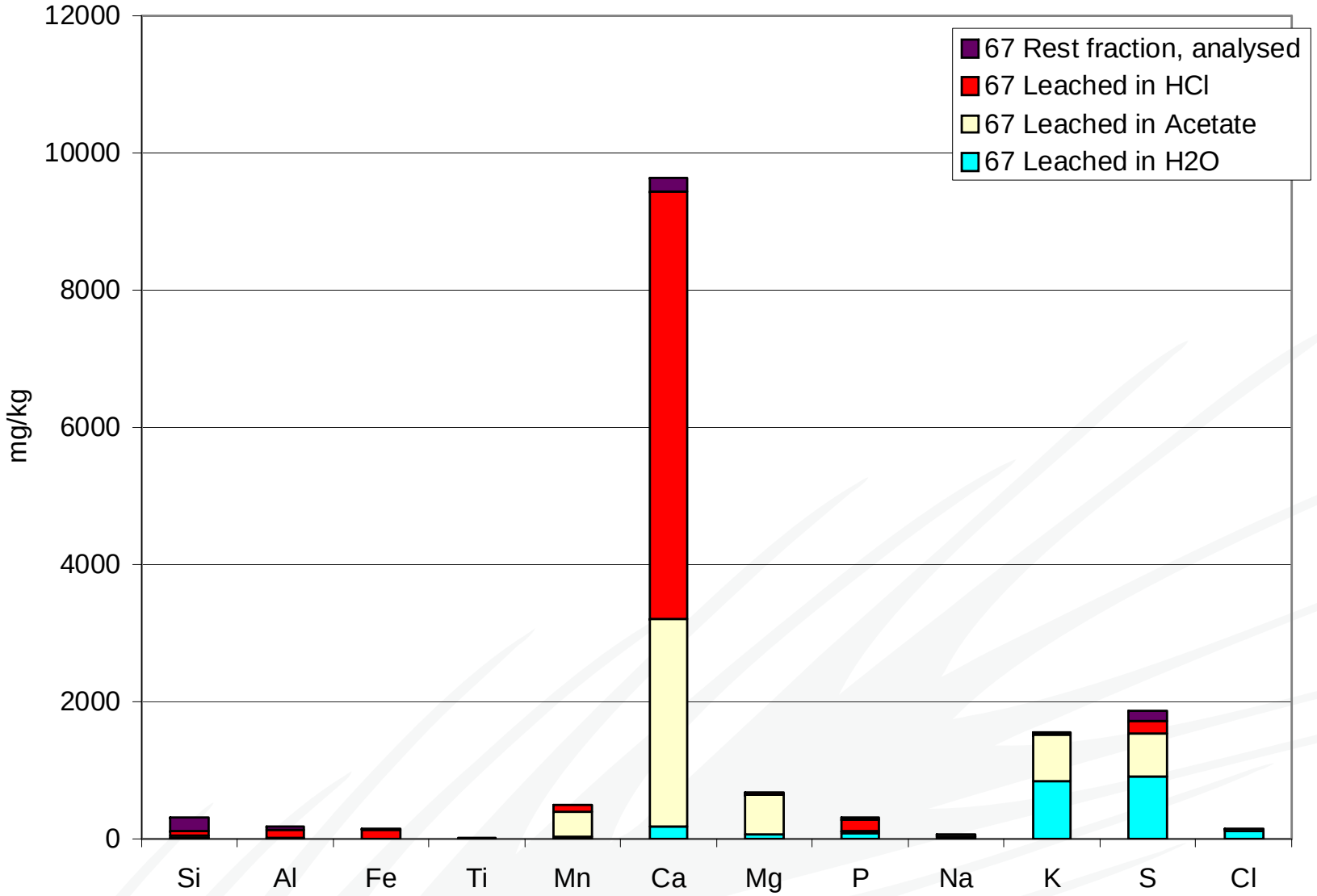
- carbonates/sulfates

Rest

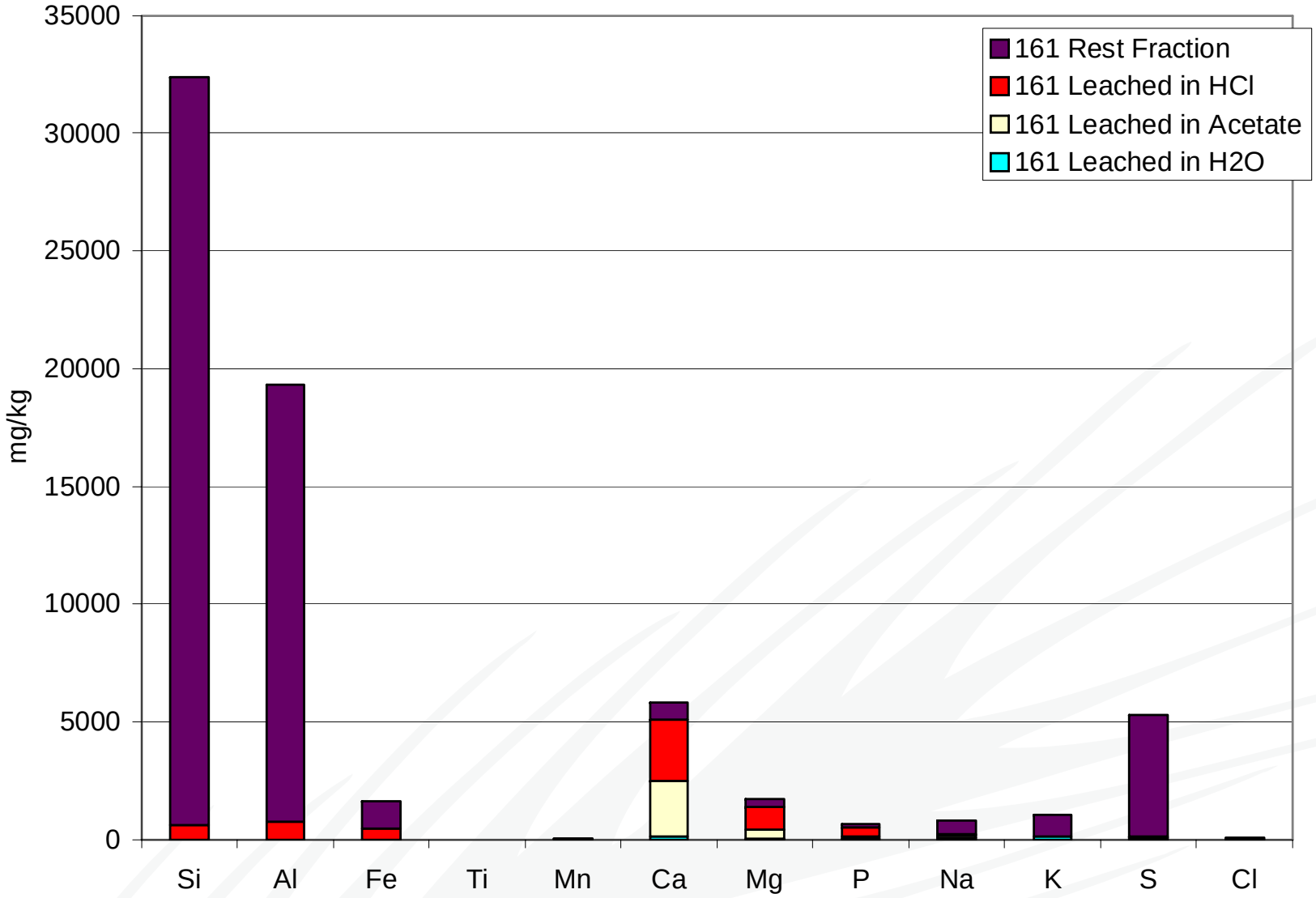
- silicates, unsoluble rest



Bark 67


12000
10000
8000
6000
4000
2000
0
mg/kg
67 Rest fraction, analysed
67 Leached in HCl
67 Leached in Acetate
67 Leached in H2O
Si
Al
Fe
Ti
Mn
Ca
Mg
P
Na
K
S
Cl

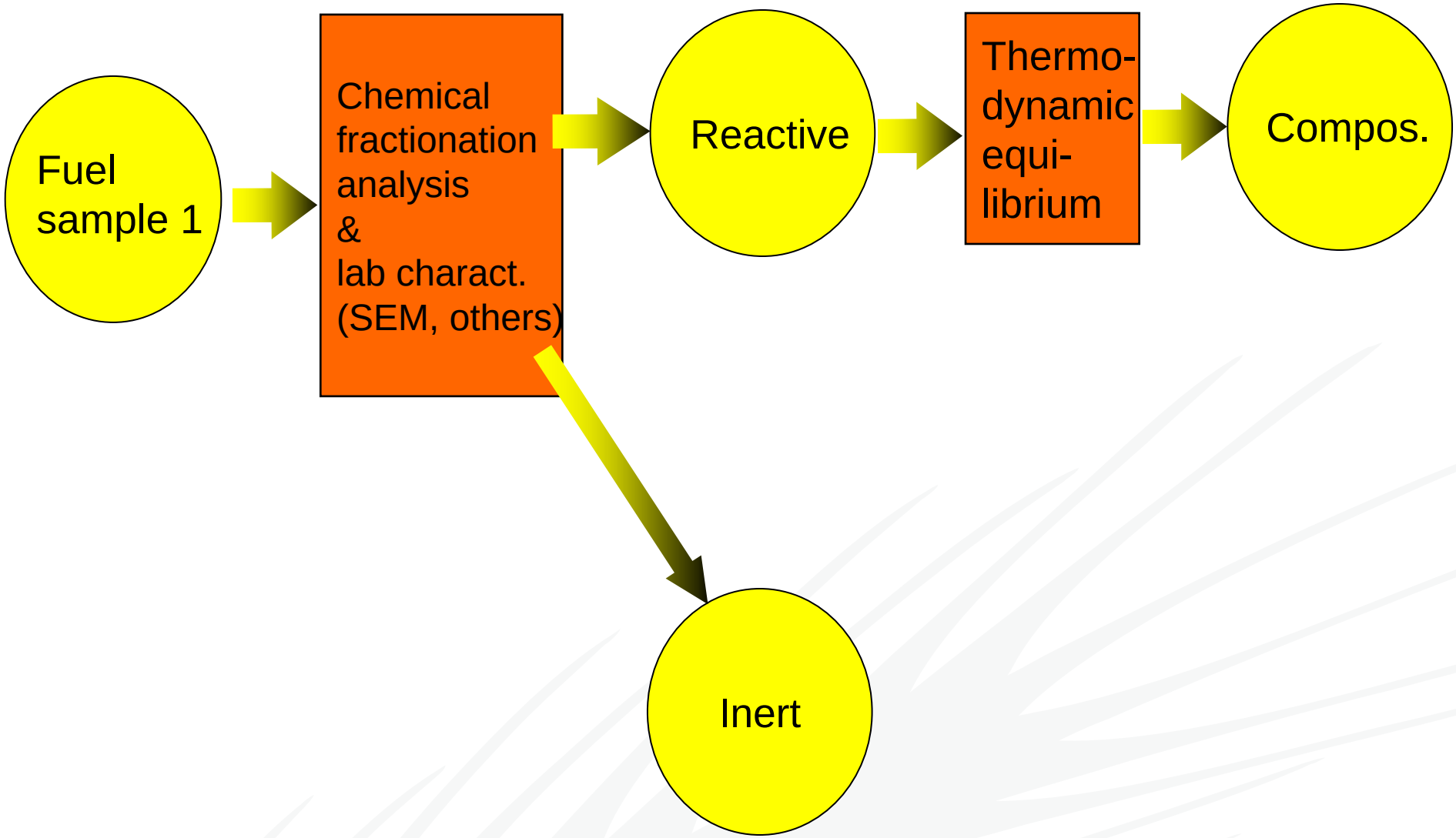
Coal 161


35000
30000
25000
20000
15000
10000
5000
0
mg/kg
161 Rest Fraction
161 Leached in HCl
161 Leached in Acetate
161 Leached in H2O
Si
Al
Fe
Ti
Mn
Ca
Mg
P
Na
K
S
Cl

Topics

- Standard laboratory ash
- Ash forming matter – advanced analysis
- Fly ash composition
- Ash melting
- Co-firng

Ash Behavior Predictions for Fuel Mixes

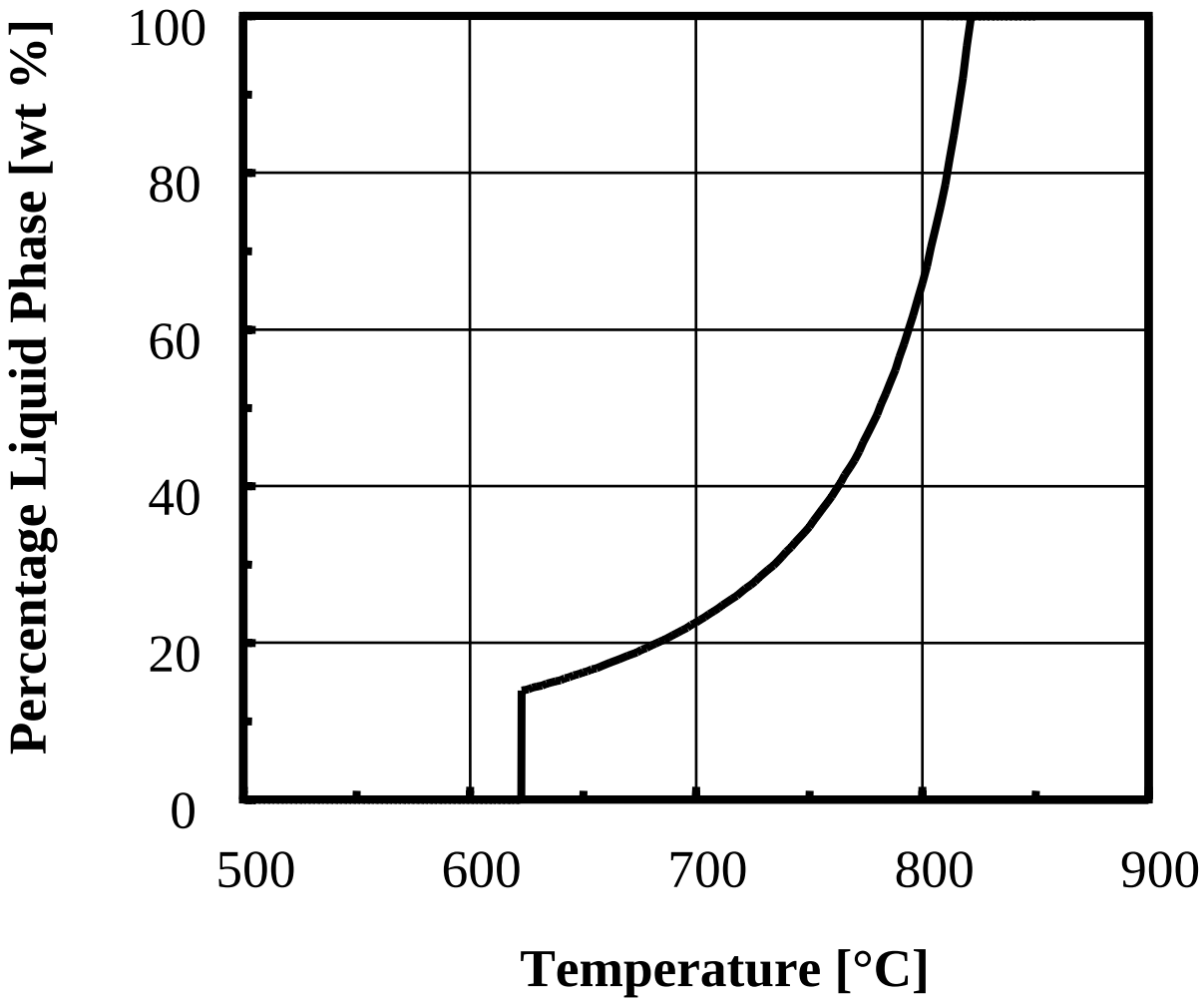


Topics

- Standard laboratory ash
- Ash forming matter – advanced analysis
- Fly ash composition
- Ash melting
- Co-firing

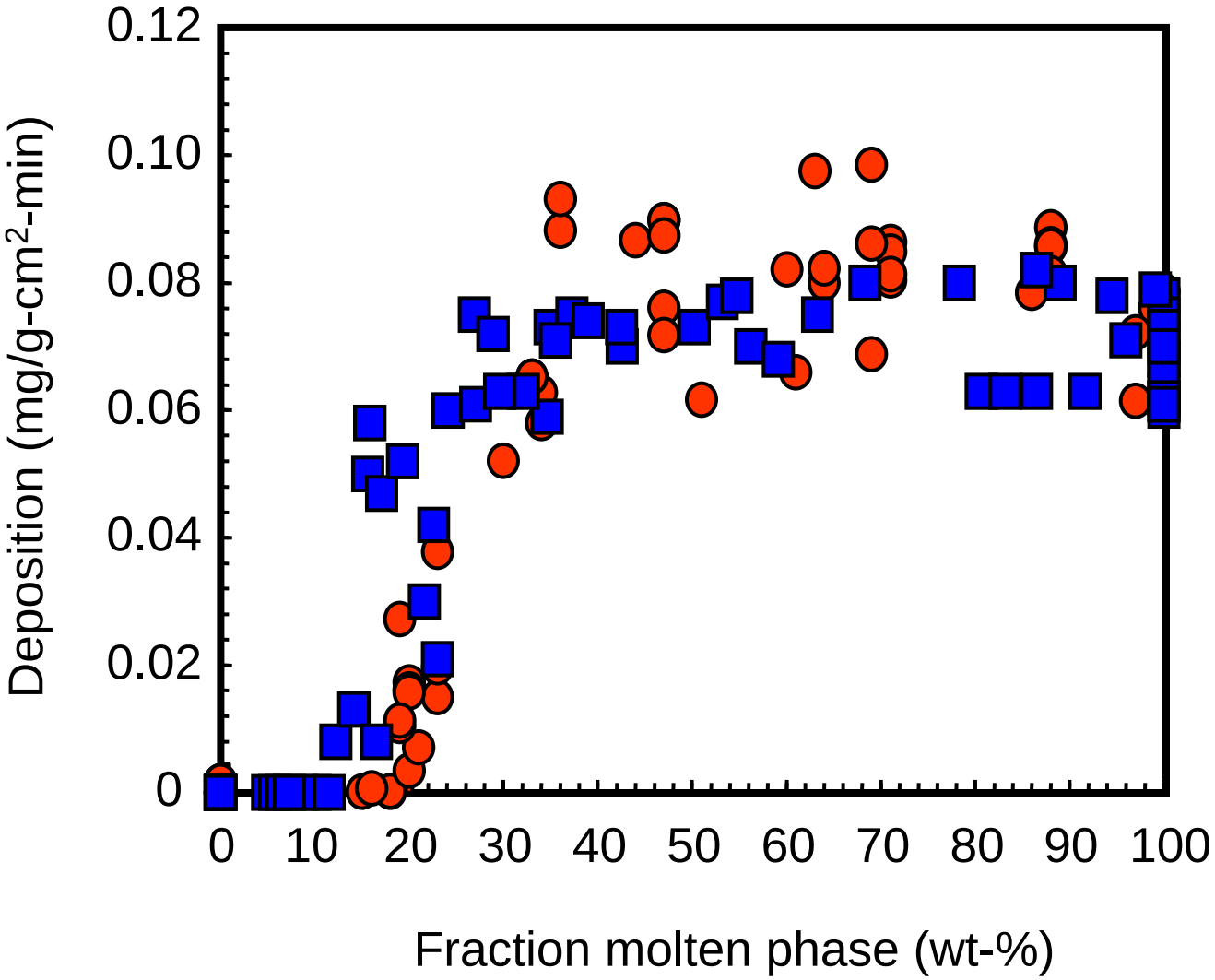
Fraction of Molten Phase vs. Temperature

Typical Superheater Deposit



Stickiness of Partially Molten Particles

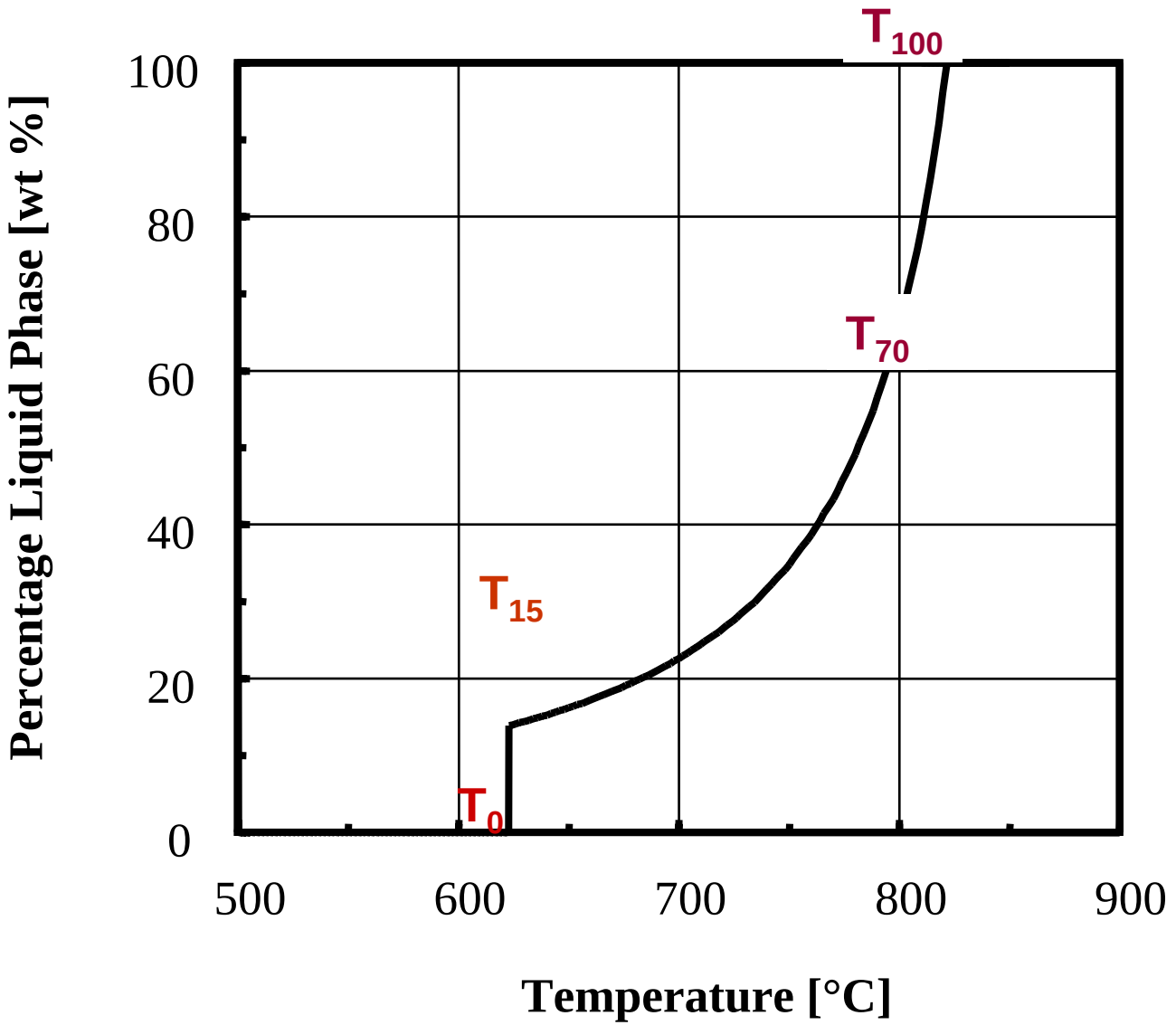
Entrained Flow Reactor Tests in Toronto



(Tran et al. 2002)

Fraction of Molten Phase vs. Temperature

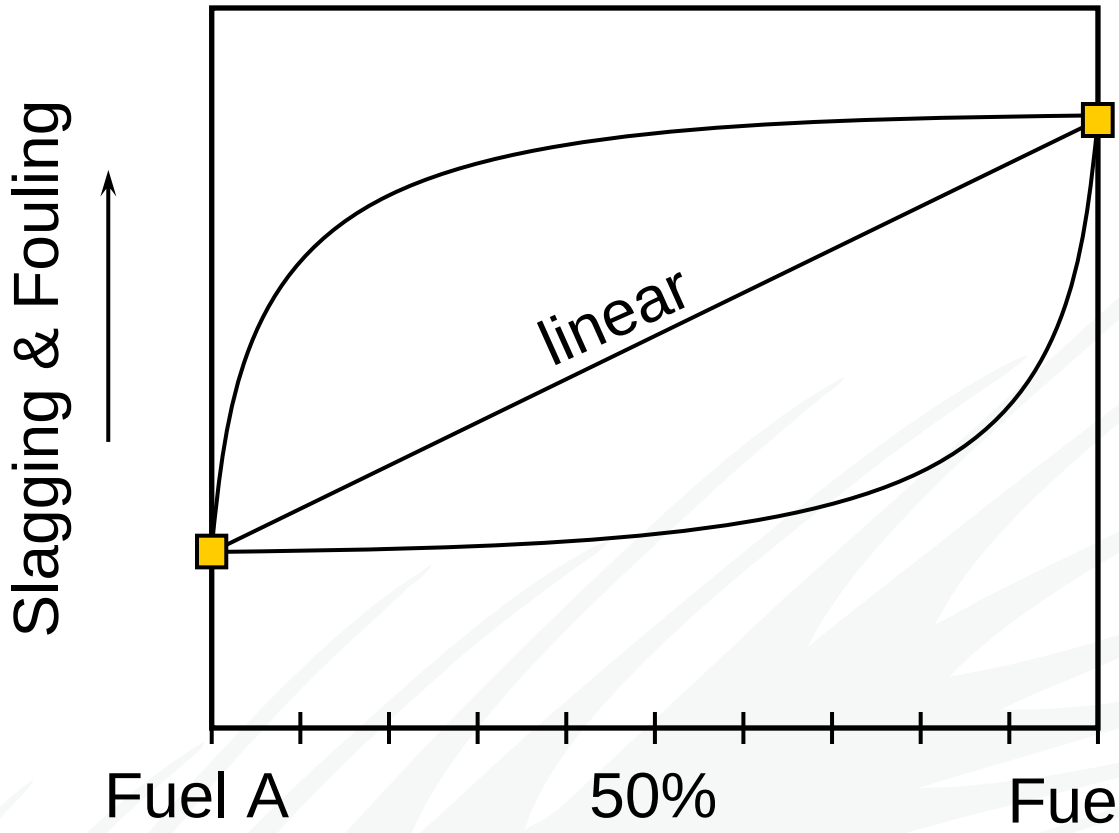
Typical Superheater Deposit



Topics

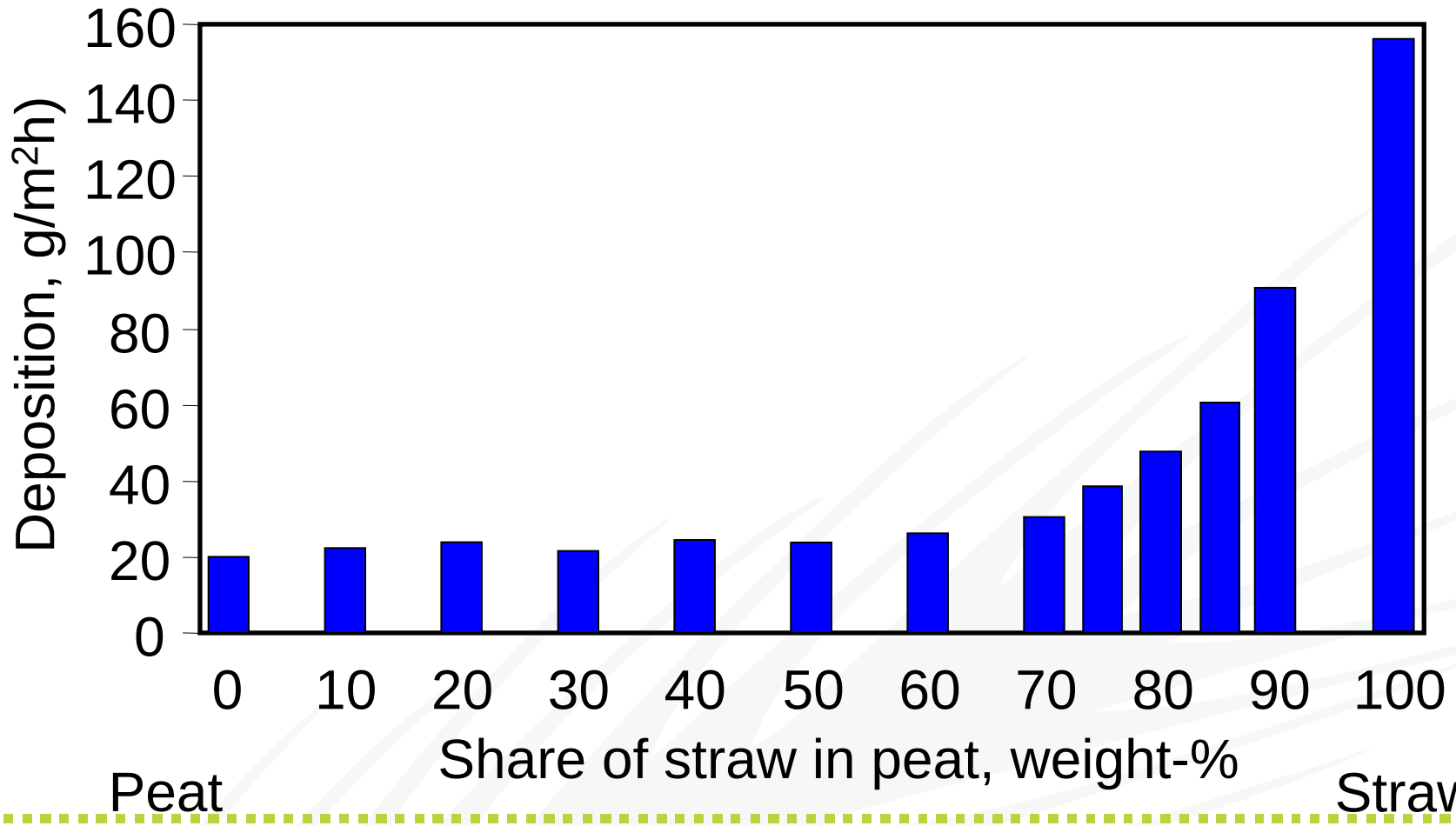
- Standard laboratory ash
- Ash forming matter – advanced analysis
- Fly ash composition
- Ash melting
- Co-firing

Co-firing, effect on slagging & fouling



/Hupa 2003; FBC plenary session/

Peat/straw co-firing lab-scale drop-tube tests

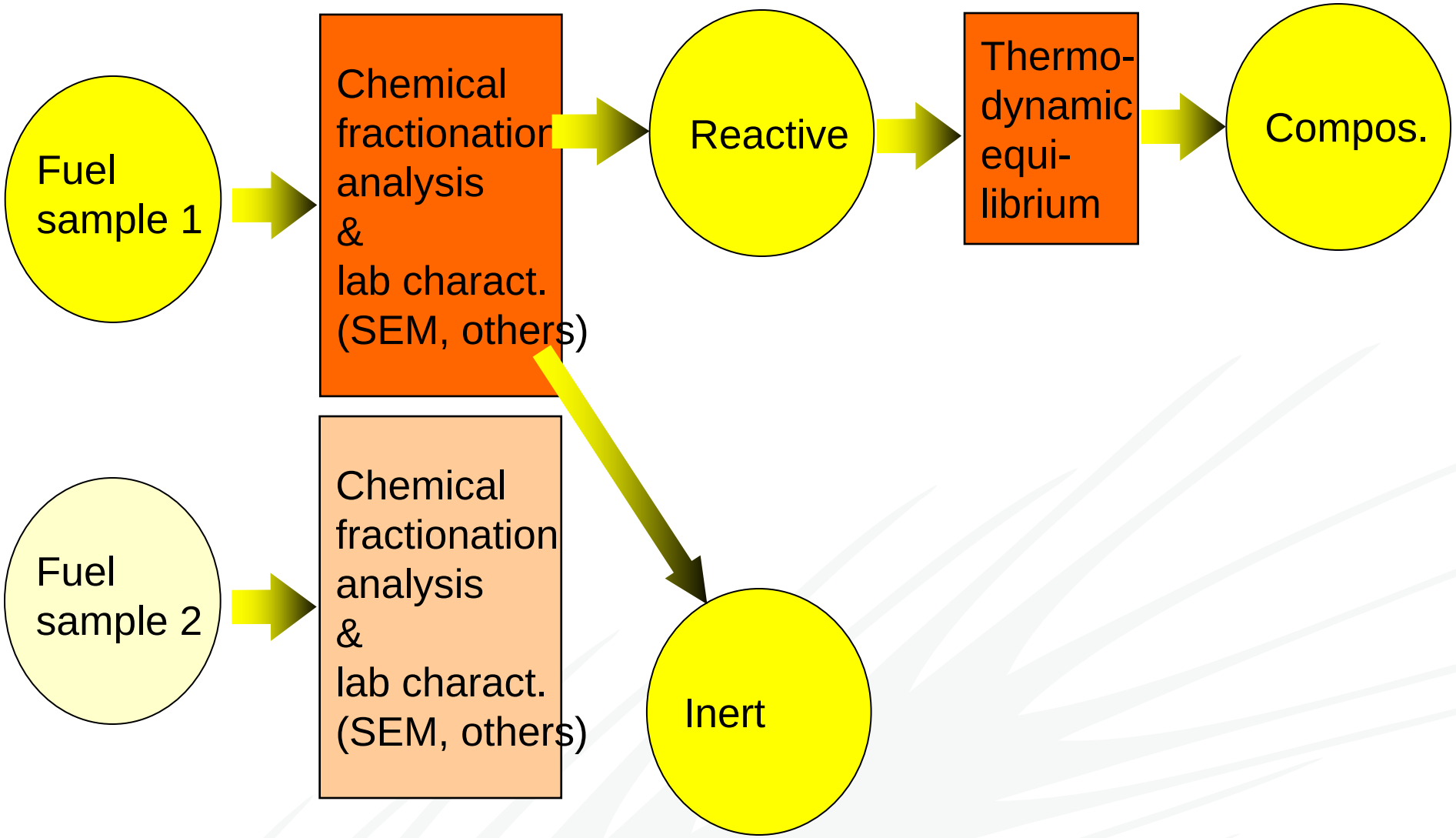


/Theis 2006; Dr thesis /

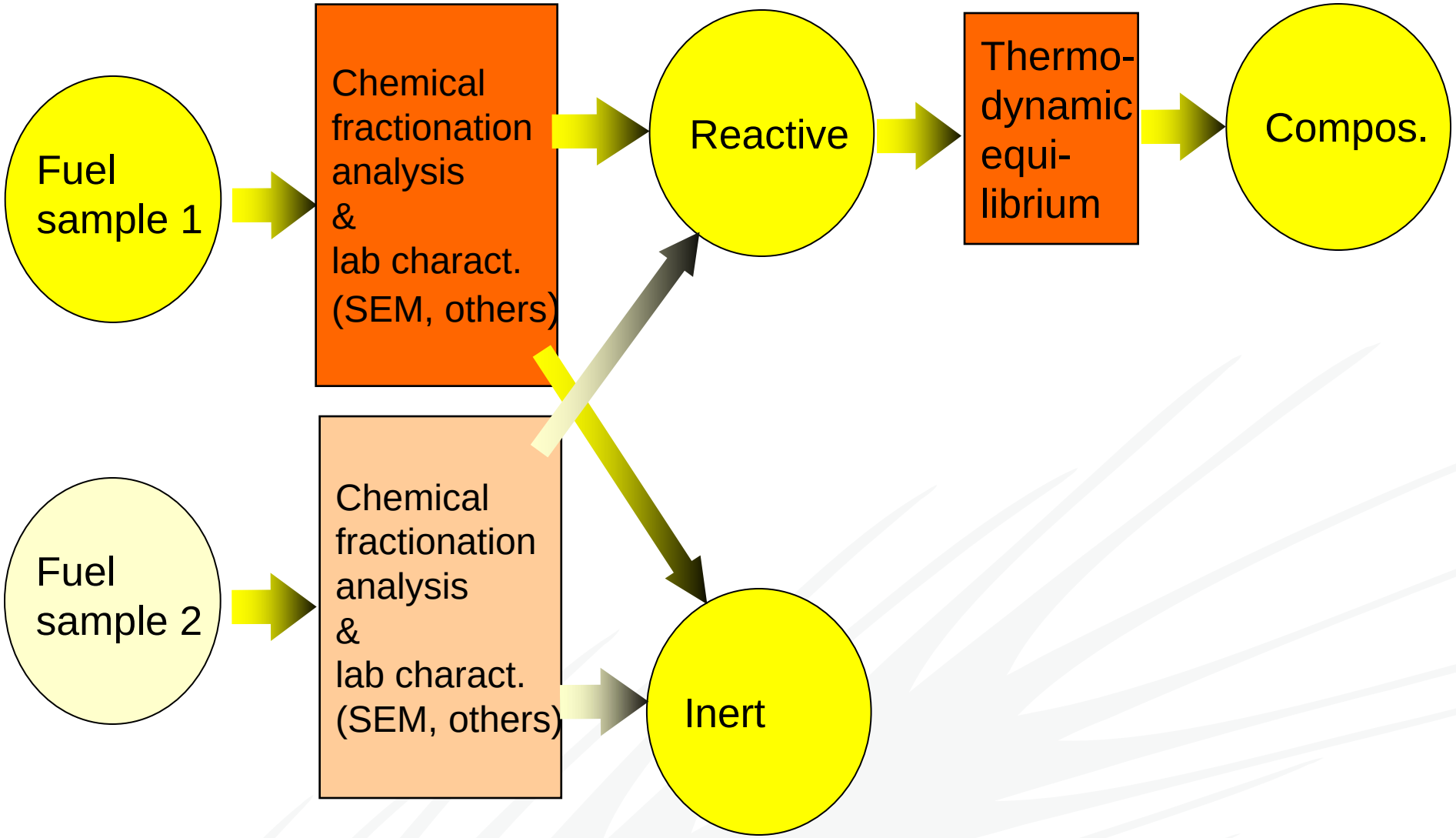
Co-firing

- Seldom a linear ash behavior
- If fuel ashes interact co-firing worse or better
- Silicate-based ashes may function as “cleaning agents”, through an erosive effect
- Sulfur may stop chlorine from getting into deposits

Ash Behavior Predictions for Fuel Mixes



Ash Behavior Predictions for Fuel Mixes



Exercises
Fuel analyses

- Chemical fractionation of fuels
  - Straw
  - Wood
- SEM/EDX of ashed fuels