9th International Conference on Circulating Fluidized Beds &
IEA-FBC Session on "Co-combustion and Ash-Related Phenomena"
May, 13 – 16, 2008
Hamburg, Germany

Ash Behavior in Fluidized Bed Combustion – Recent Research Highlights

Mikko Hupa
Åbo Akademi University
Turku, Finland

- Ash Forming Matter
- Fly Ash Formation
- Bed Reactions
- Fouling
- Corrosion

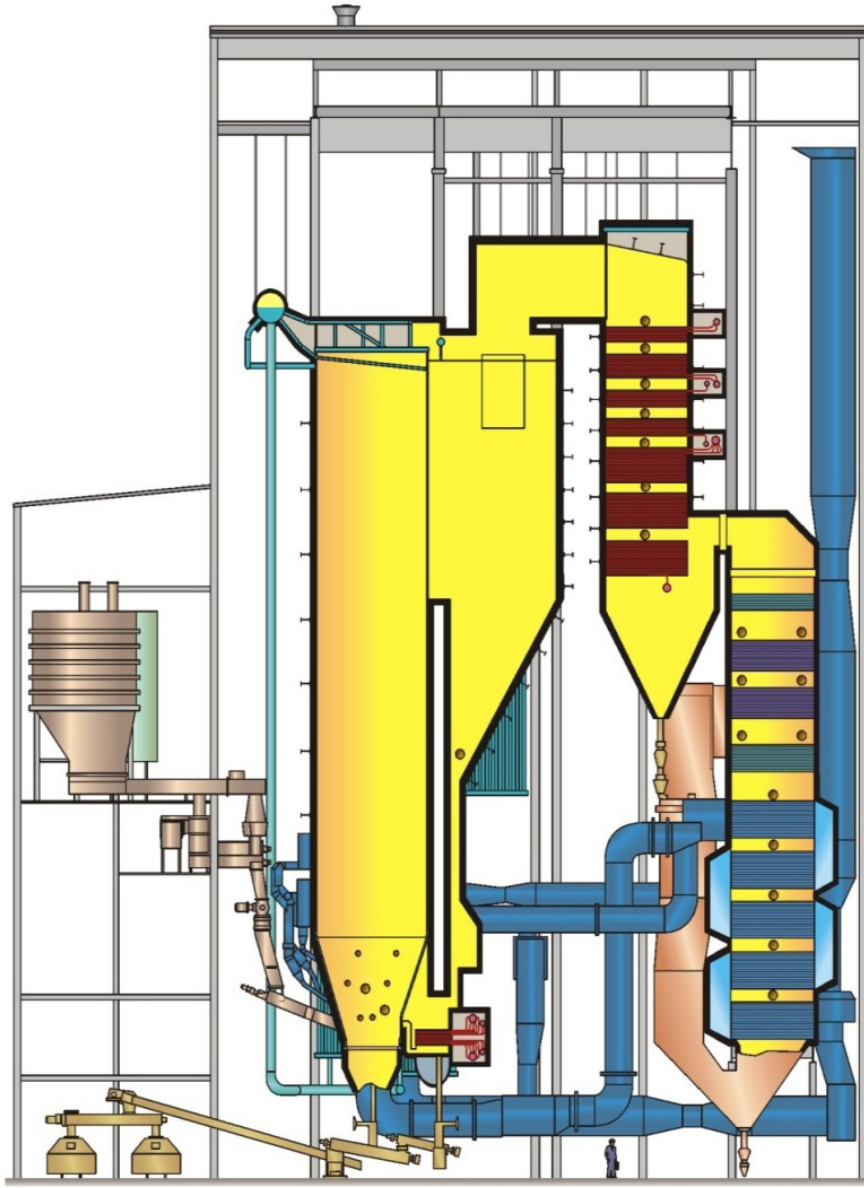
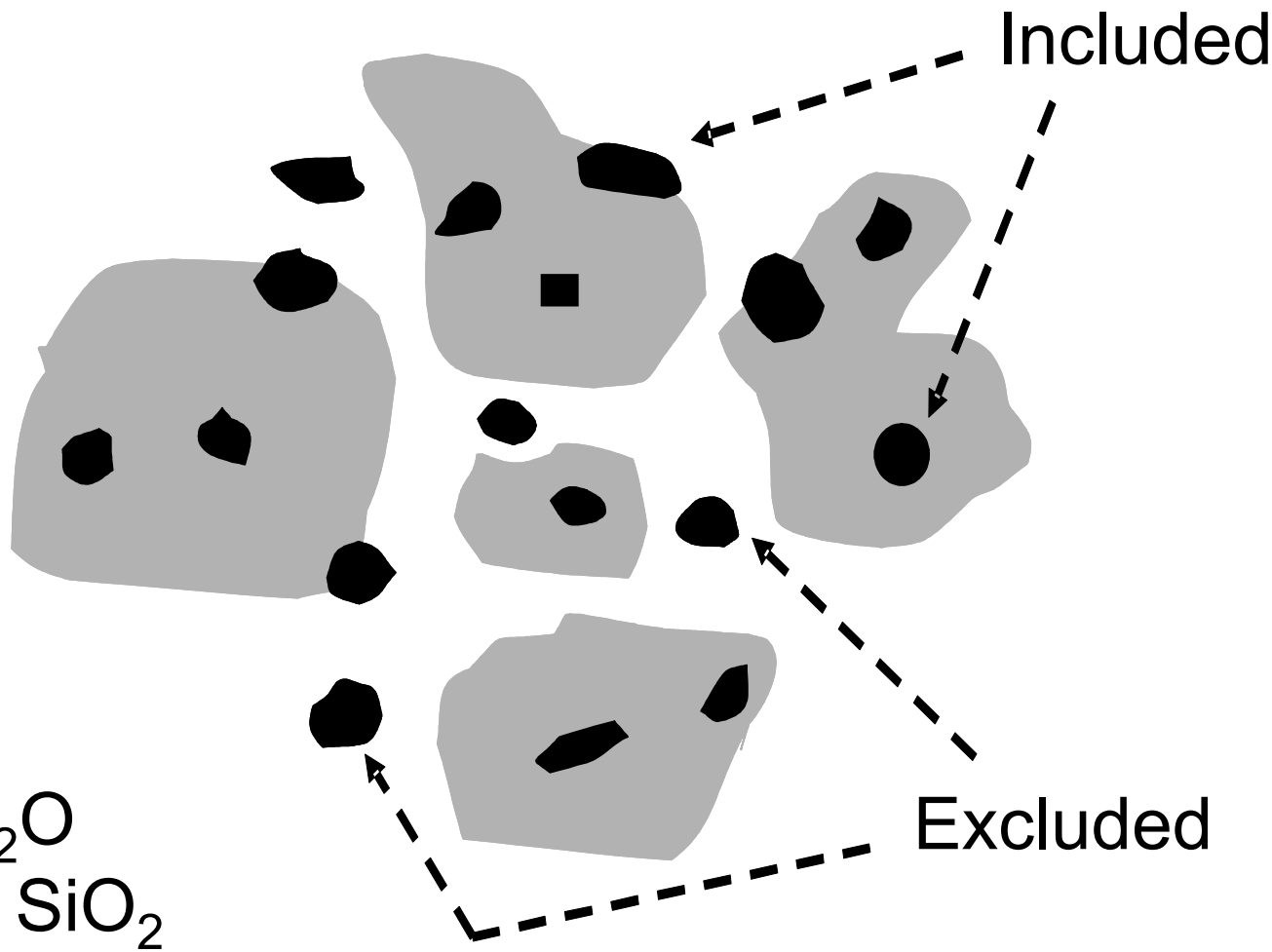


Figure courtesy: Mälarenergi Ab & Foster Wheeler

Standard Ash Analysis of Some Fuels

		Coal	**Peat**	**Forest residue**	***Salix***
Ash	% db	13.6	7.5	2.1	2.1
SiO_2	%wt in ash	54.7	22.6	18.8	17.0
Al_2O_3	“	21.9	20.1	1.1	6.7
Fe_2O_3	“	8.1	27.6	0.7	1.5
TiO_2	“	0.9		0.1	0.1
MnO	“	0.1		1.7	
CaO	“	4.5	8.6	35.7	30.6
MgO	“	1.9	2.7	4.4	3.5
Na_2O	“	0.7	0.4	5.5	0.2
K_2O	“	0.7	0.5	0.2	26.0
P_2O_5	“	2.3	2.7	9.8	15.5
SO_3	“			2.2	3.2
CO_2	“			19.2	
Cl	“	0.1		0.1	0.7
SUM		95.9	85.2	100.6	107.1

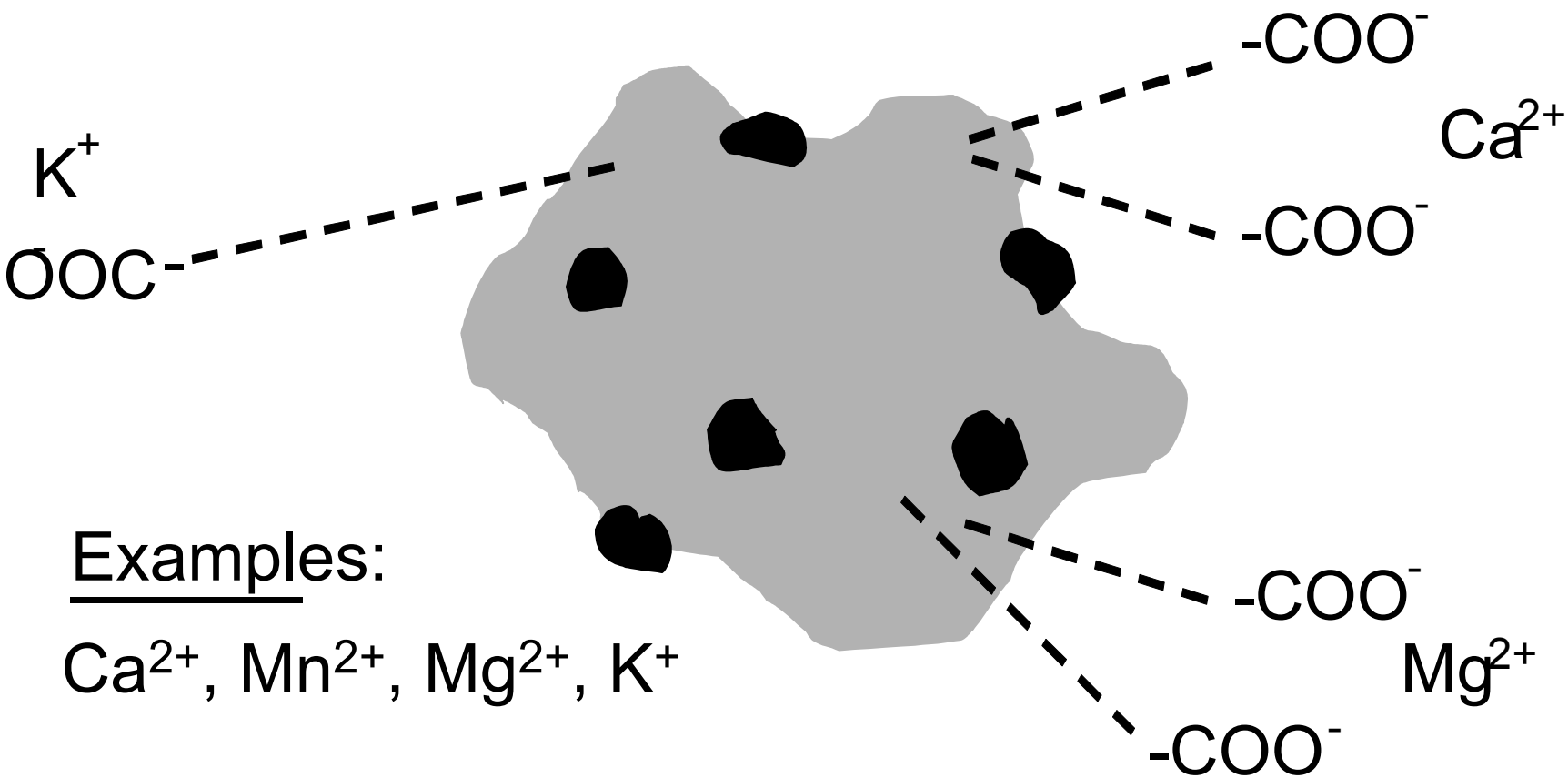
Ash in Biomass Fuels: Included and Excluded Minerals



Examples:

$CaC_2O_4 \cdot 2H_2O$
Amorphous SiO_2

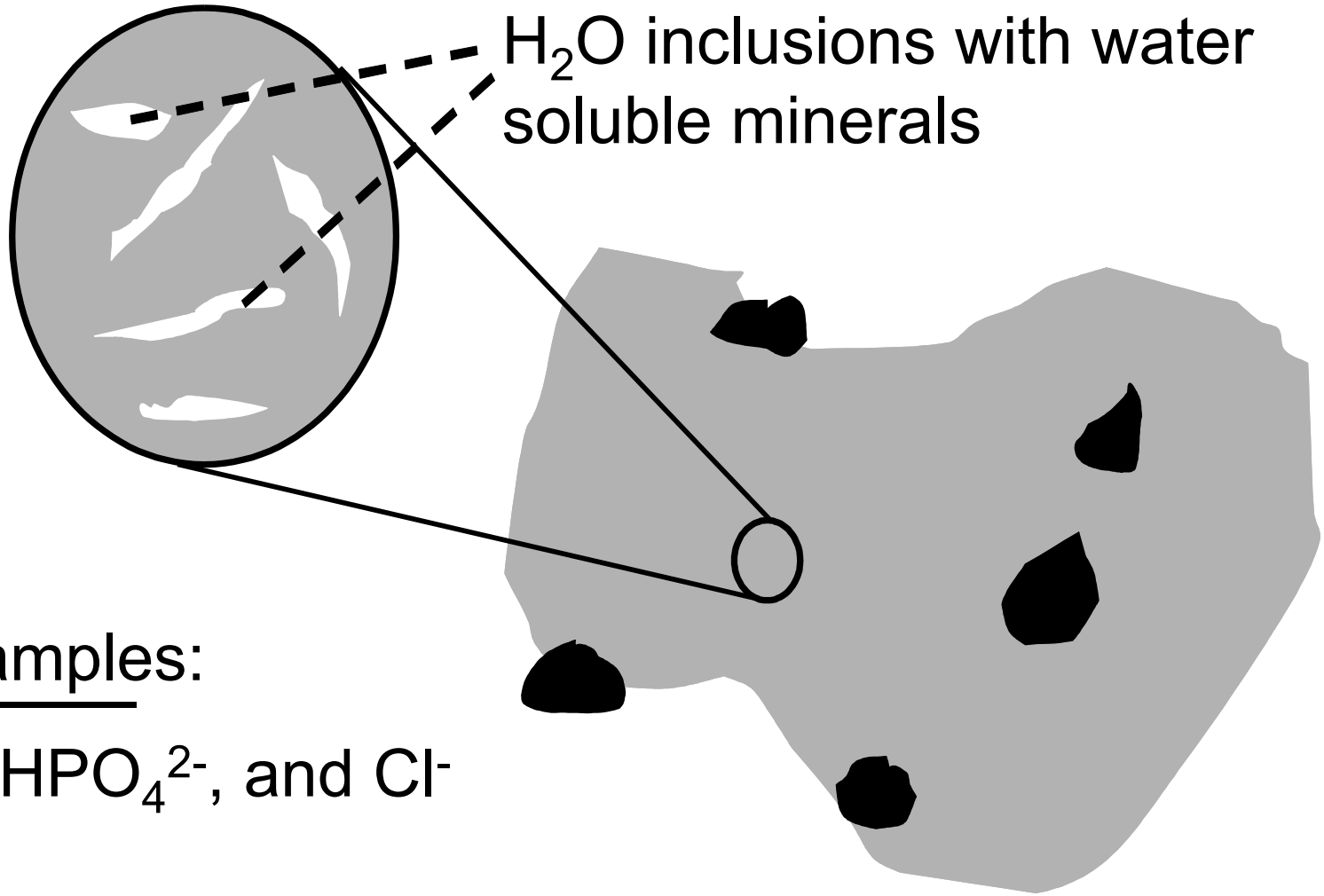
Ash in Biomass Fuels: Organically Associated Metals



Examples:

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

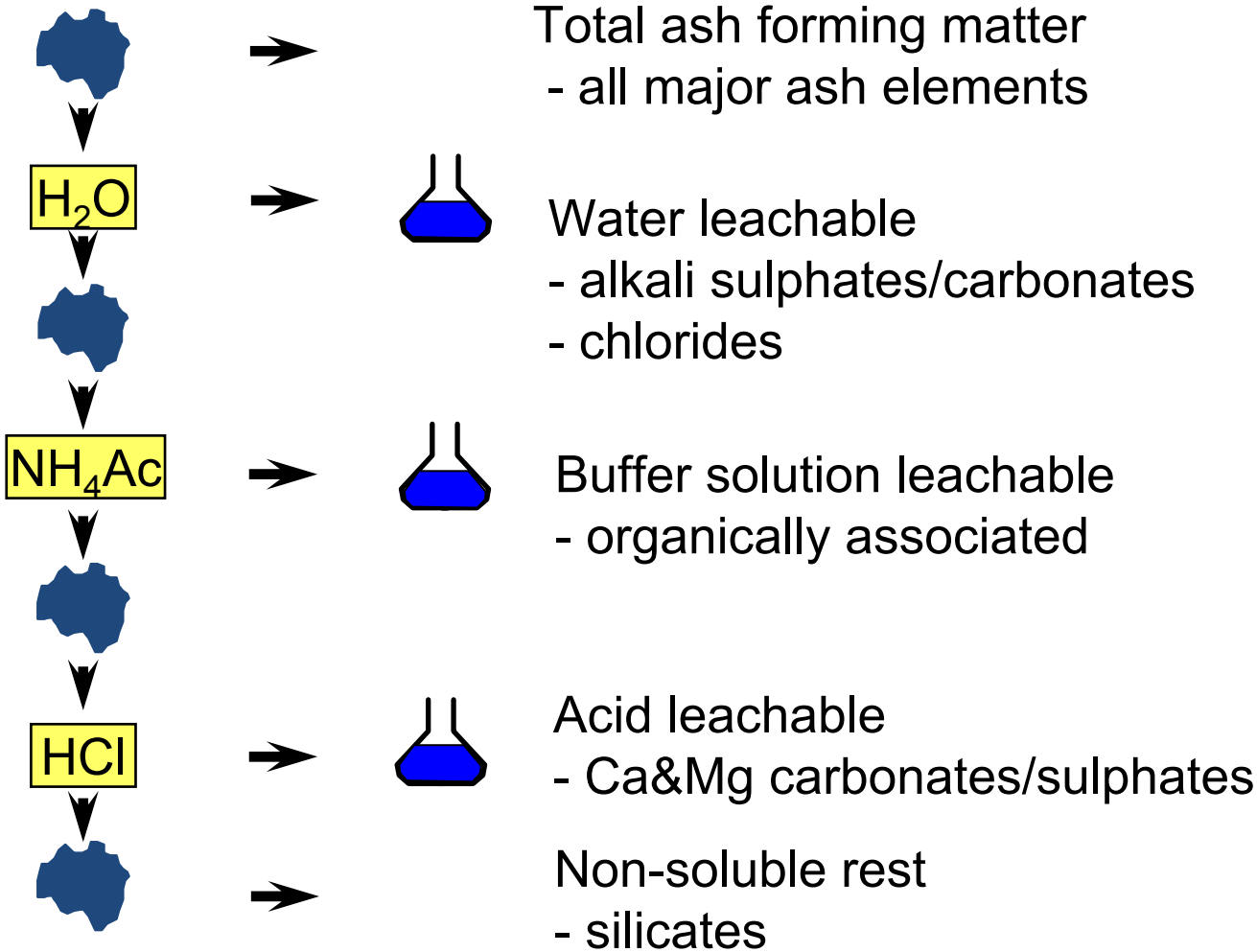
Ash in Biomass Fuels: Ions in Aqueous Solutions



Examples:

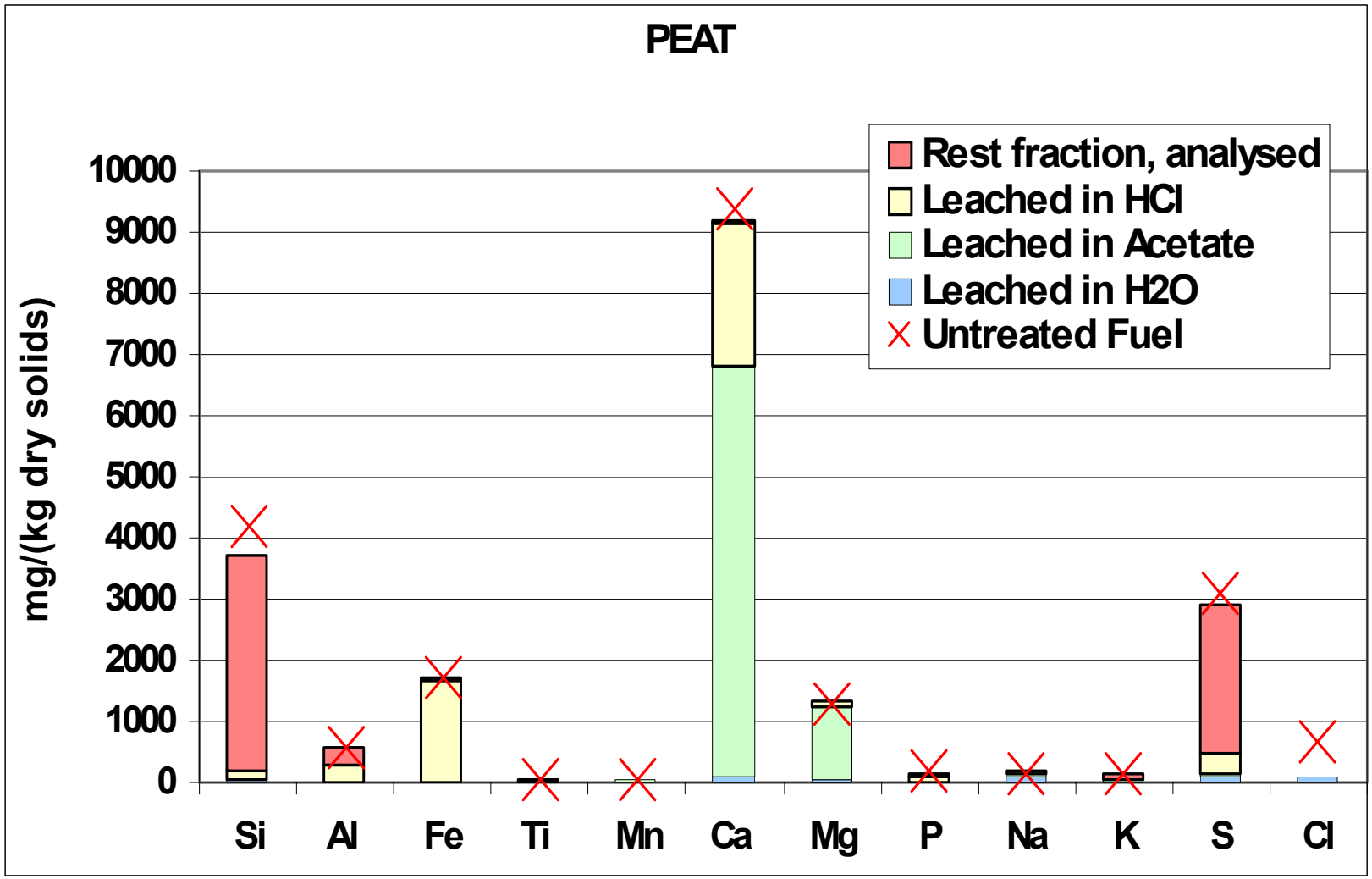
K^+, HPO_4^{2-}, and Cl^-

Chemical Fractionation by Stepwise Leaching

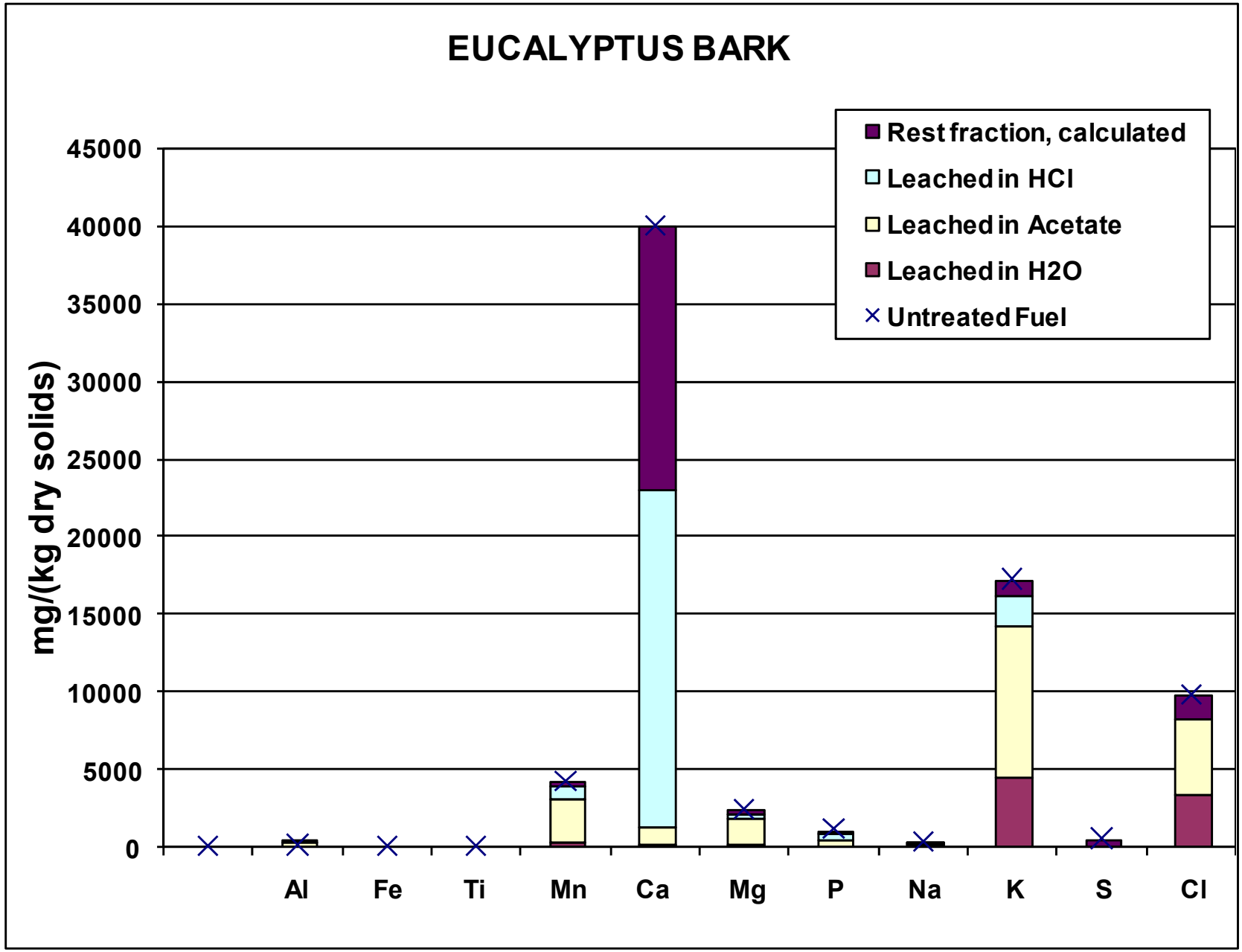


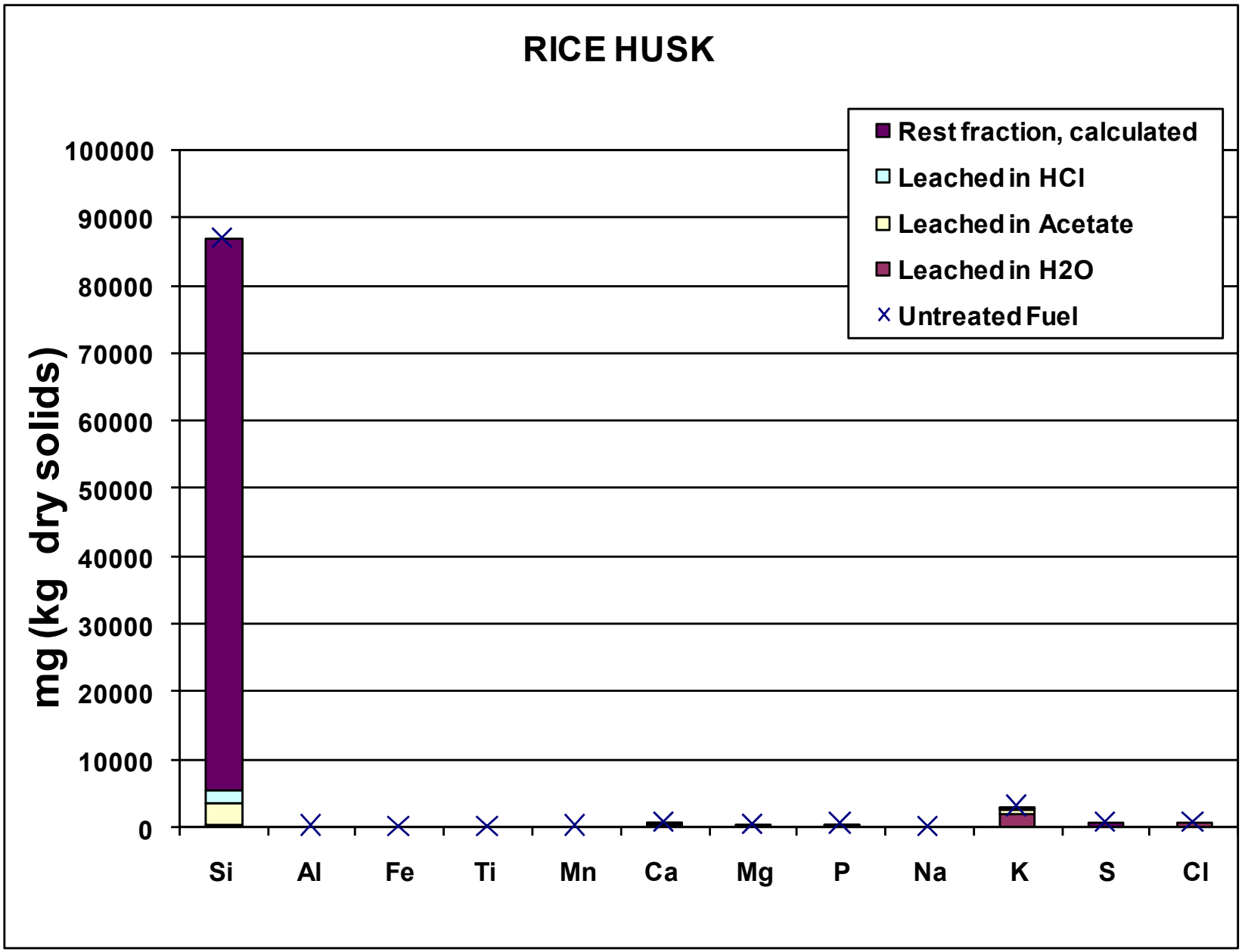
Benson & Holm 1985, Zevenhoven 2000

Chemical Fractionation - Peat

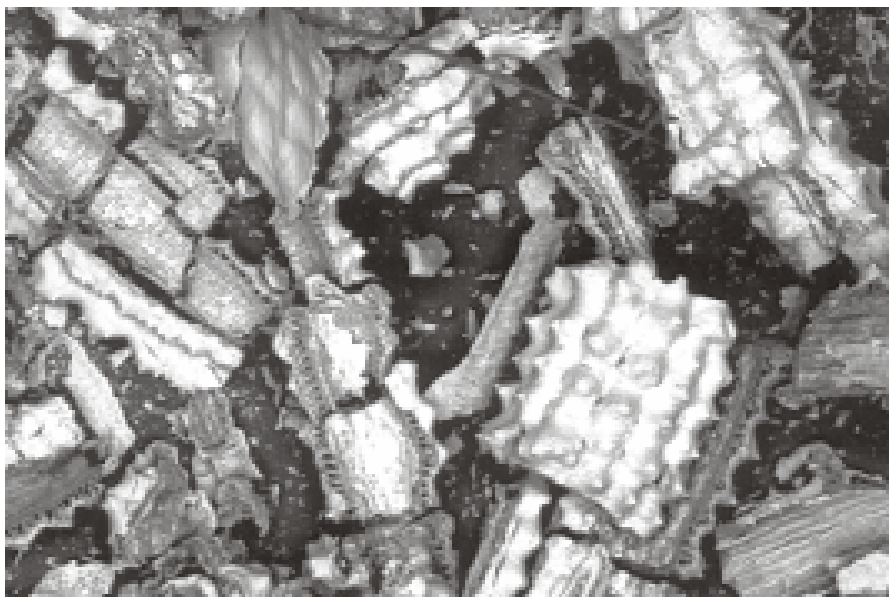


Chemical Fractionation: Bark




RICE HUSK
Rest fraction, calculated
Leached in HCl
Leached in Acetate
Leached in H2O
Untreated Fuel
mg (kg dry solids)
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
Si
Al
Fe
Ti
Mn
Ca
Mg
P
Na
K
S
Cl

Slow Ashing
Rice Husk (500 C)



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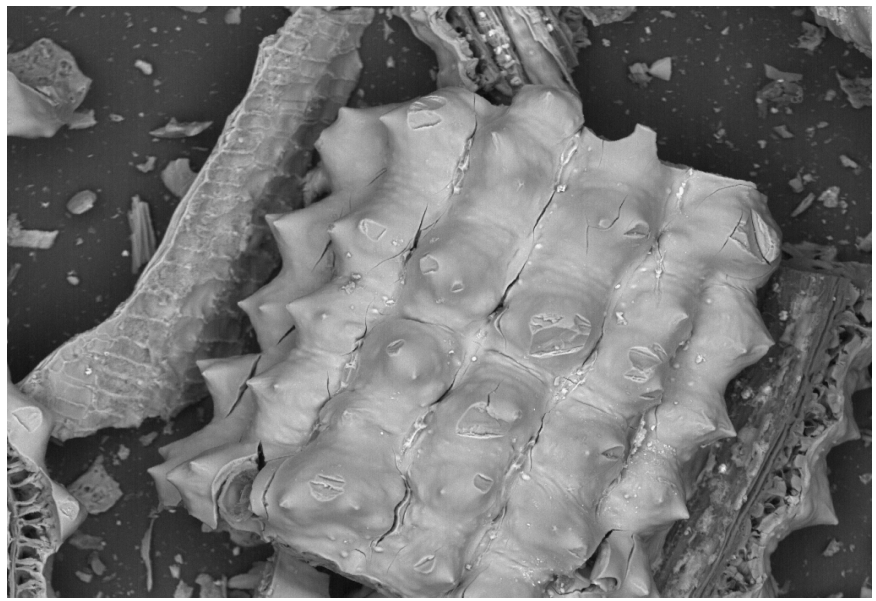
200 µm



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100 µm

(Skrifvars et al. 2005)

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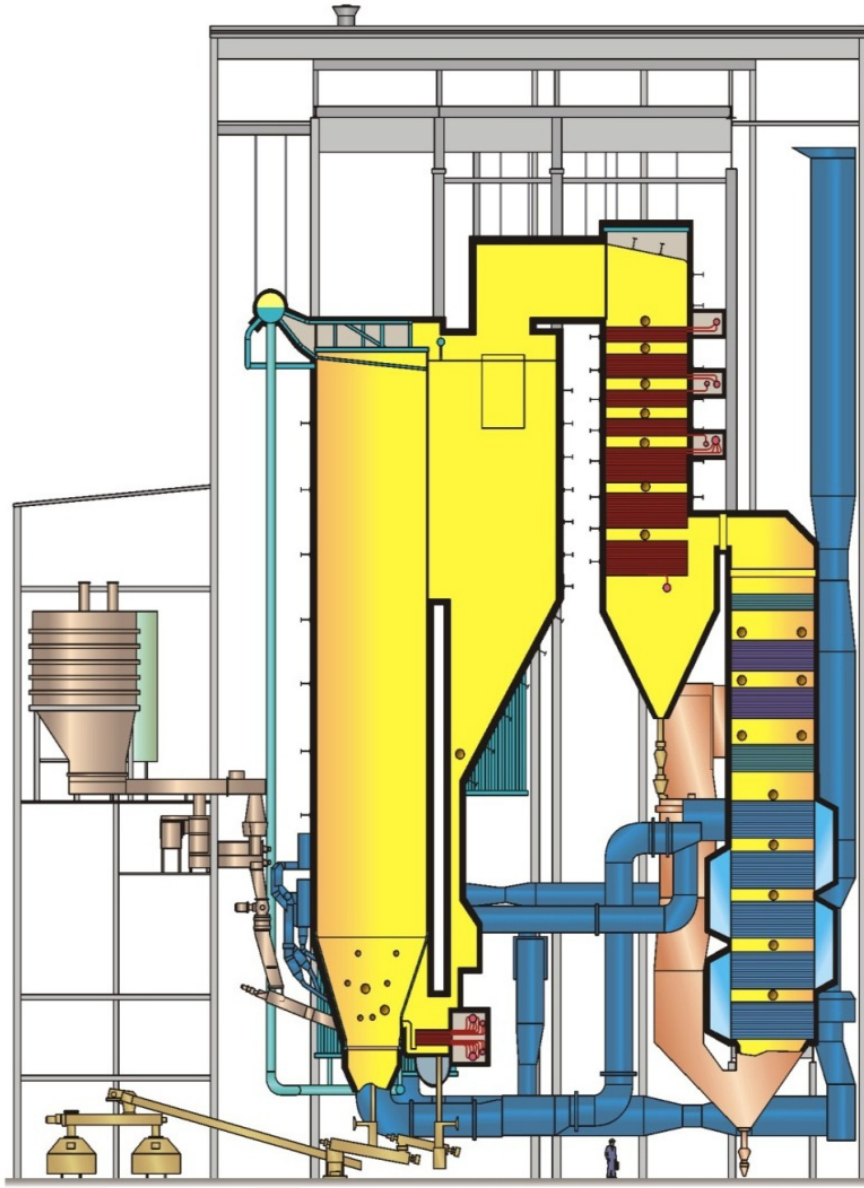
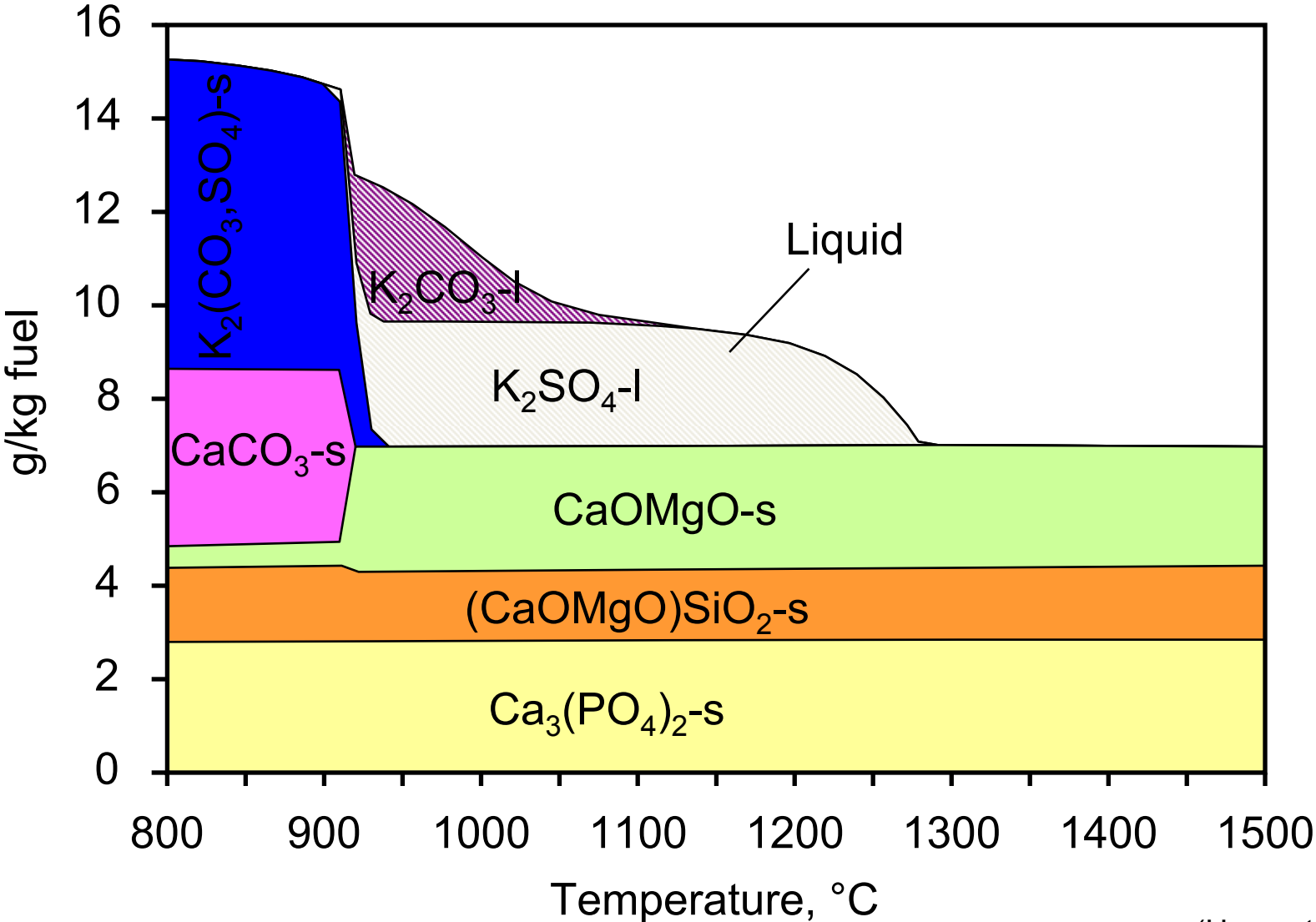


Figure courtesy: Mälarenergi Ab & Foster Wheeler

Fly Ash Composition of *Salix*

Multicomponent Multiphase Thermodynamic Calculation



(Hupa et al. 1999)

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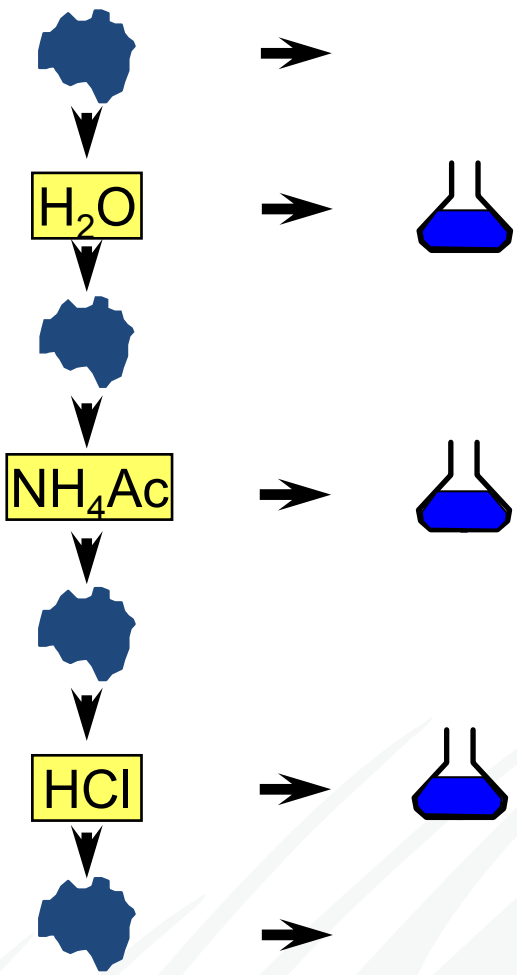
Chemical Fractionation by Stepwise Leaching



Total ash forming matter
- all major ash elements

Water leachable
- alkali sulphates/carbonates
- chlorides

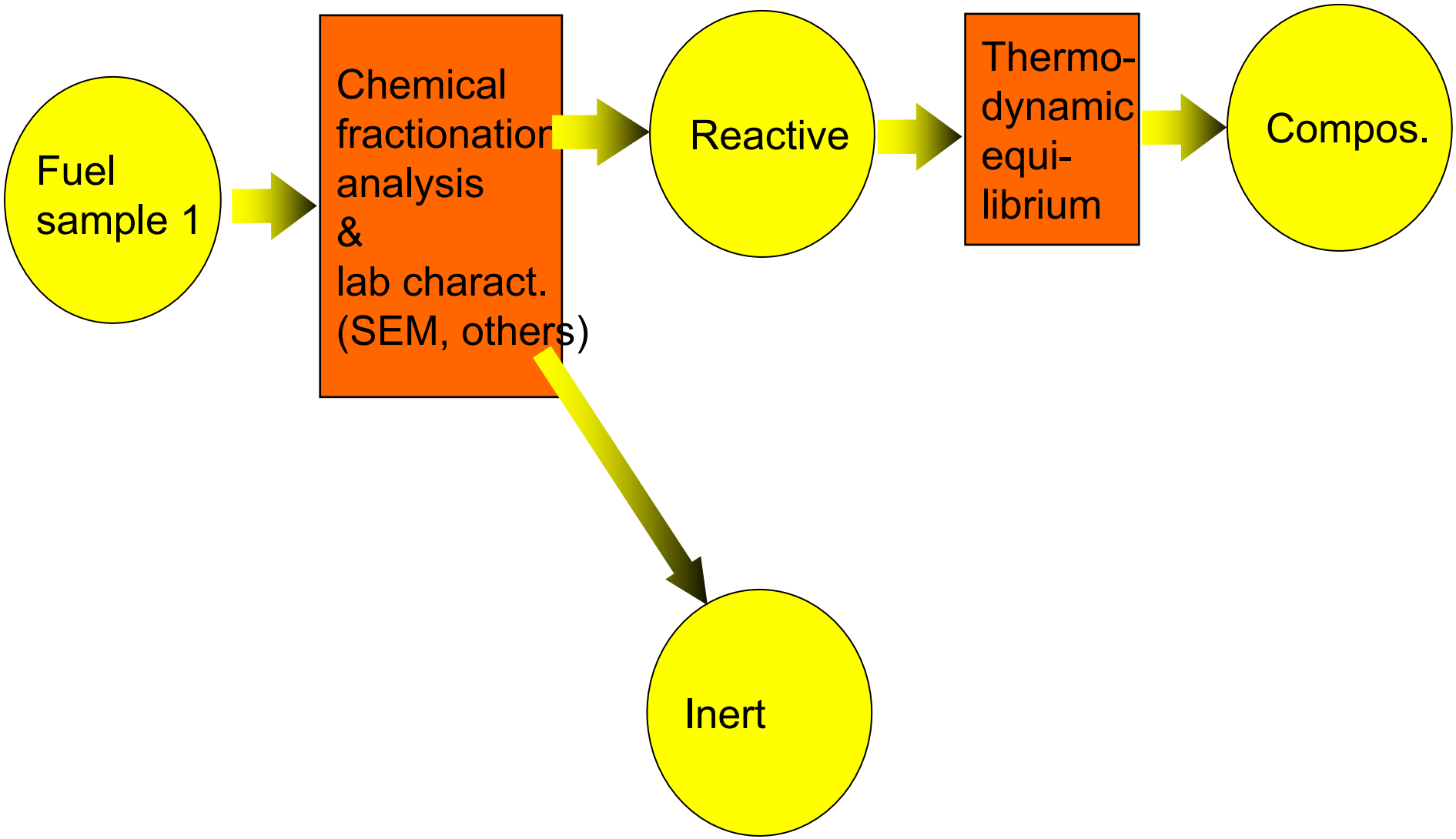
Buffer solution leachable
- organically associated

Acid leachable
- Ca&Mg carbonates/sulphates

Non-soluble rest
- silicates

Benson & Holm 1985, Zevenhoven 2000

Ash Behavior Predictions for Fuel Mixes



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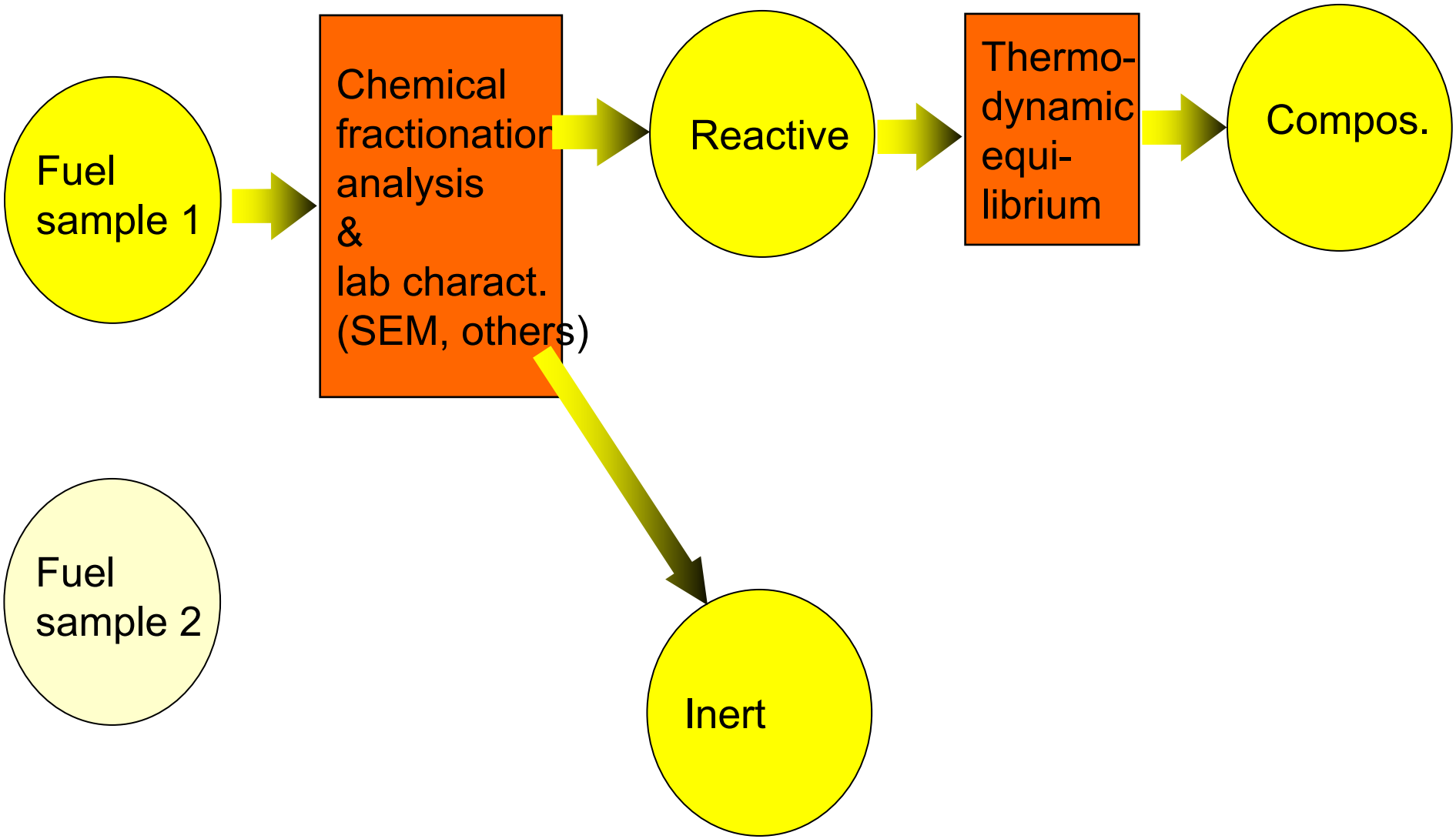

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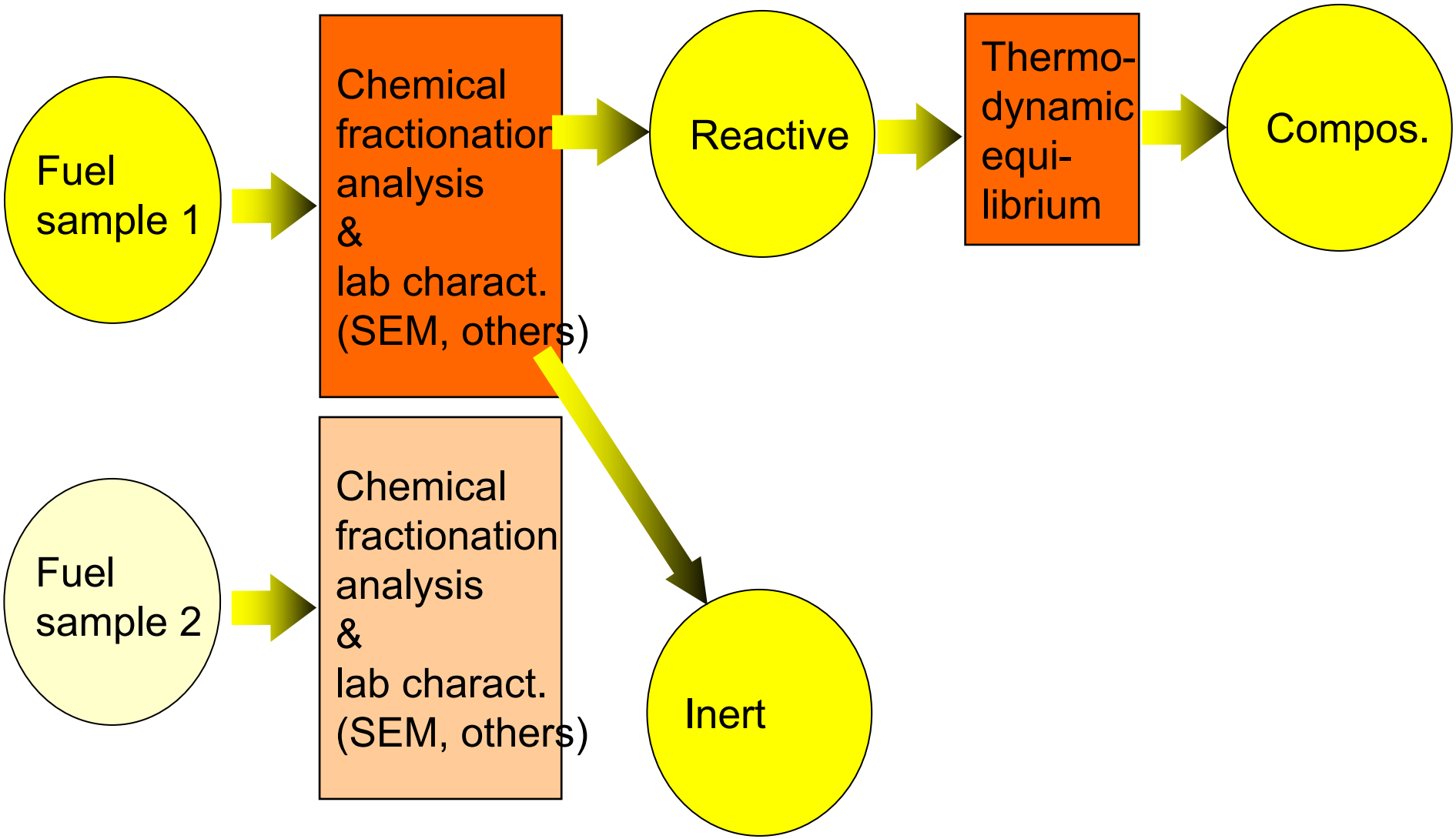

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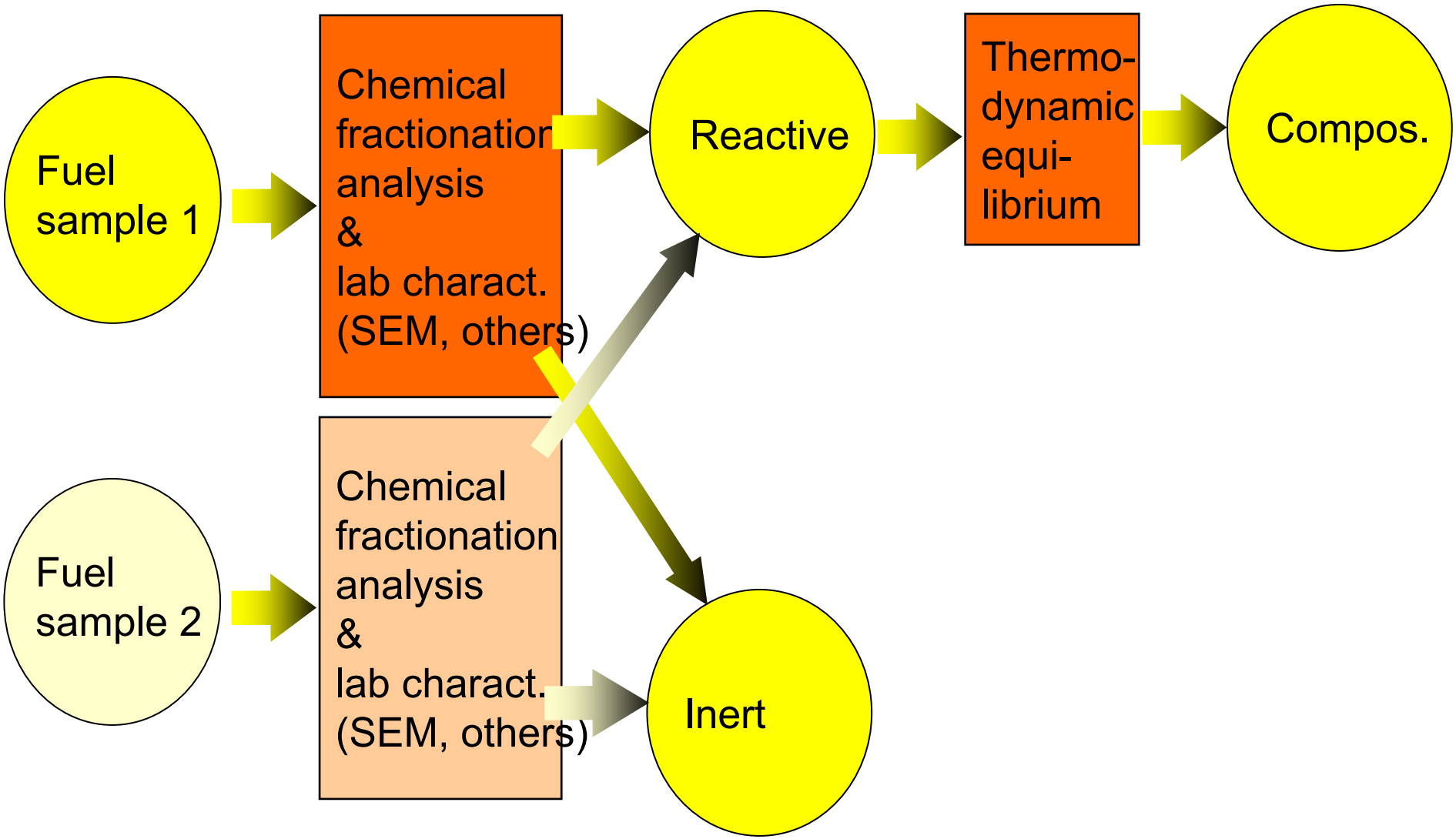

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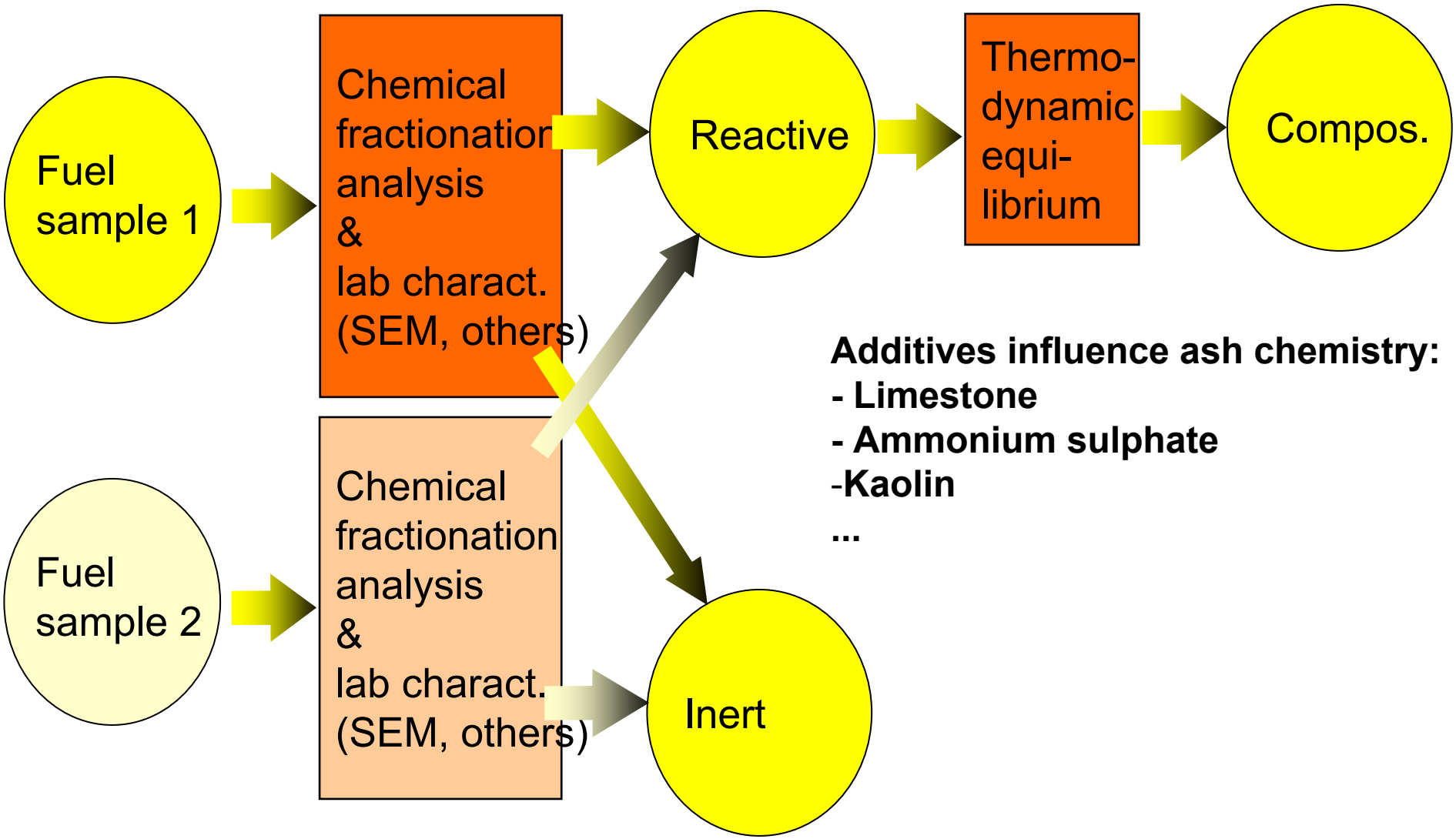


Additives influence ash chemistry:
- Limestone
- Ammonium sulphate
-Kaolin
...

- Ash Forming Matter
- Fly Ash Formation
- Bed Reactions
- Fouling
- Corrosion

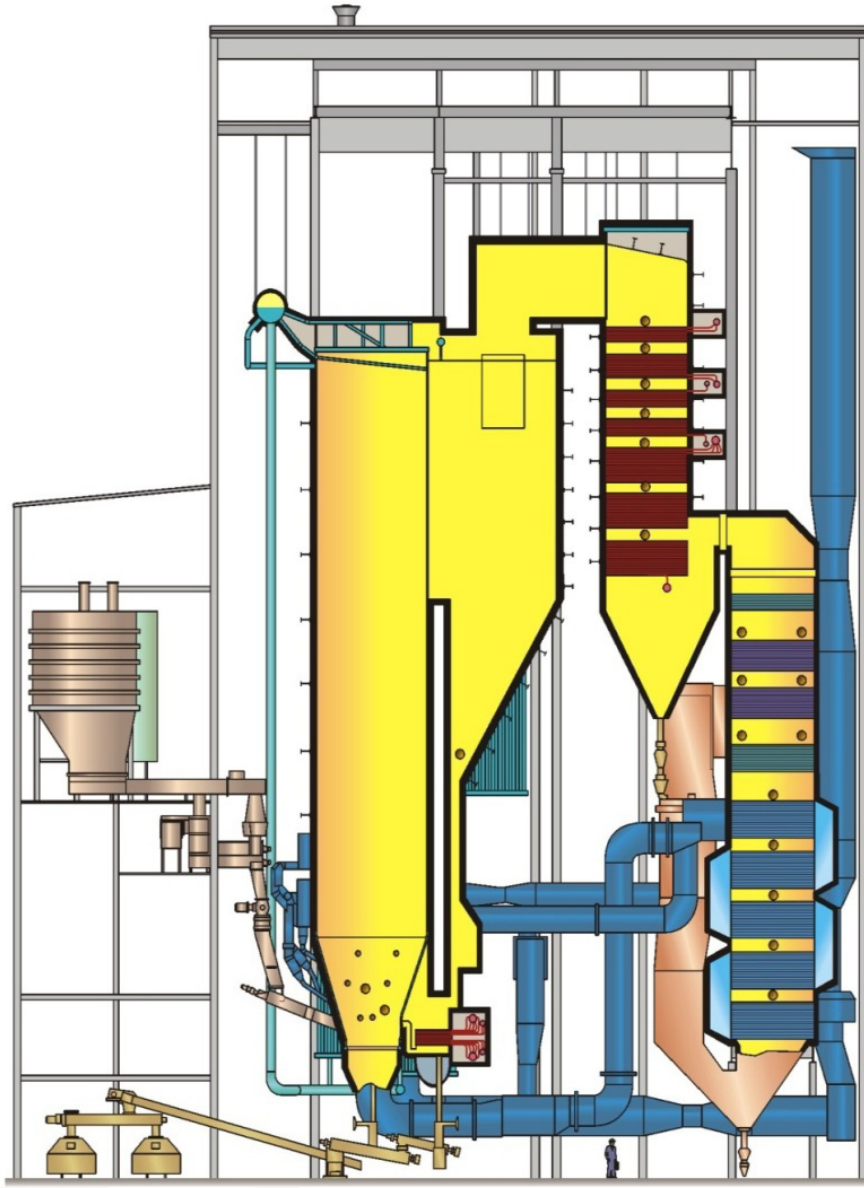
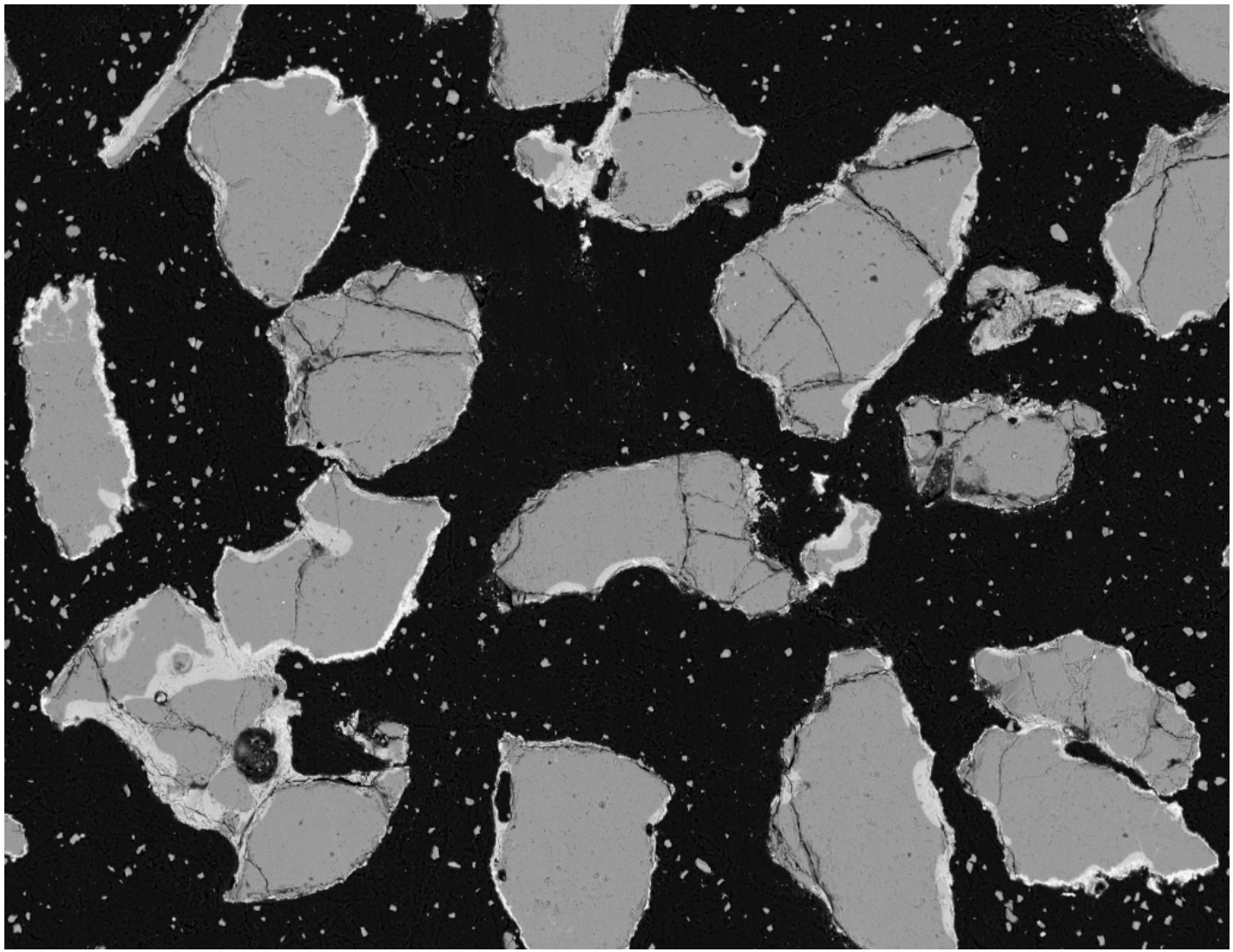


Figure courtesy: Mälarenergi Ab & Foster Wheeler

Alkali Silicate Coating on Bed Particles after Combustion with Sawdust



(Zevenhoven et al. 2006)

Bed Sintering Chemistry

- Reactions with alkali vapors:

$SiO_2(s) + 2\ KCl(g) + H_2O(g) = K_2SiO_3(l) + 2\ HCl(g)$

$SiO_2(s) + 2\ KOH(g) = K_2SiO_3(l) + H_2O(g)$

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- Reactions with calcium oxide and hydrogen chloride:

$CaO(s) + 2\ HCl(g) = CaCl_2(l) + H_2O(g)$

$SiO_2(s) + 2\ CaCl_2(l) + H_2O(g) = CaSiO_3(s) + 2\ HCl(g)$

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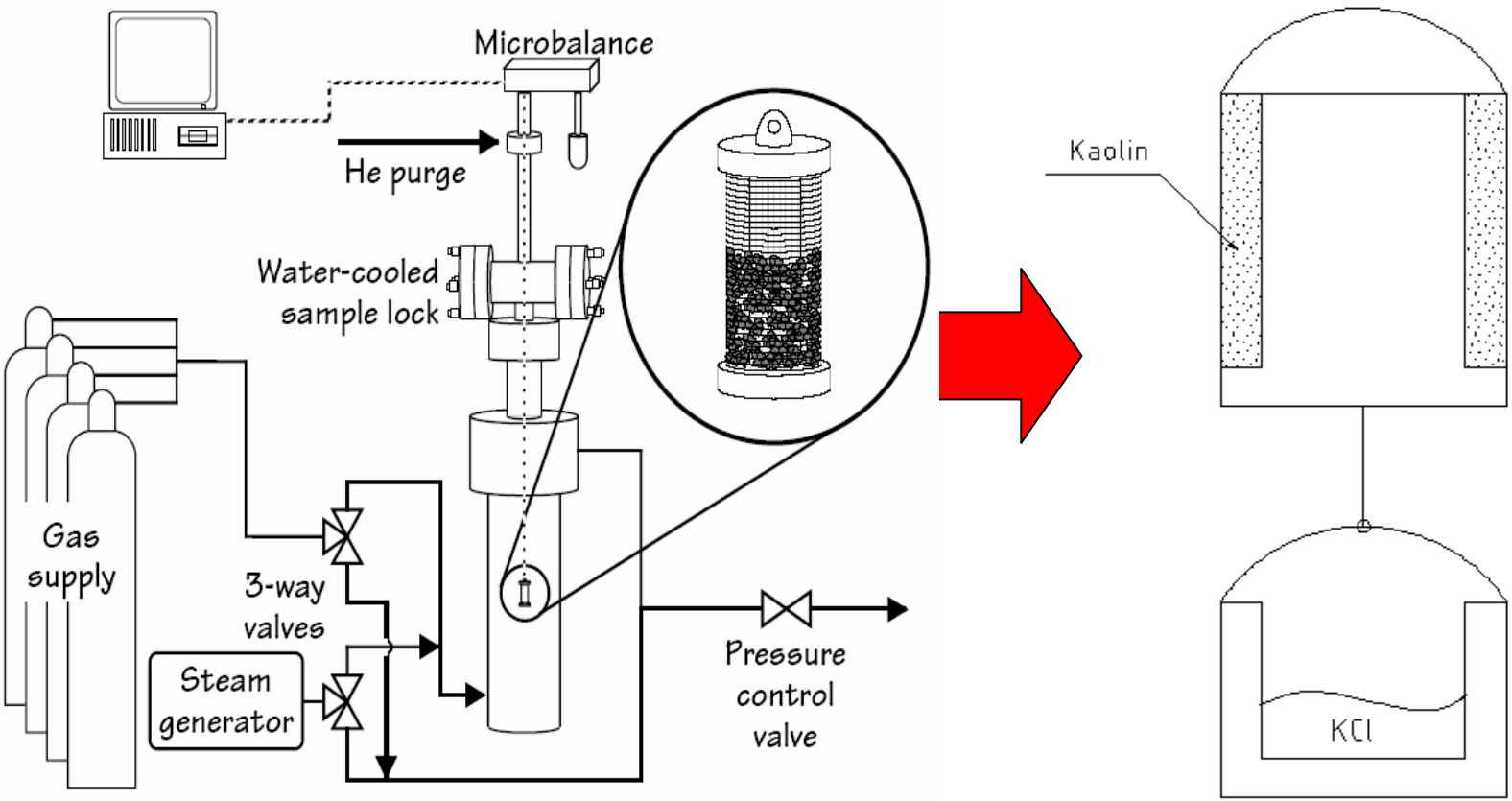
- Reactions with alkali phosphates

KCl(g) – Kaolin Reaction (TGA measurements at 800 C)

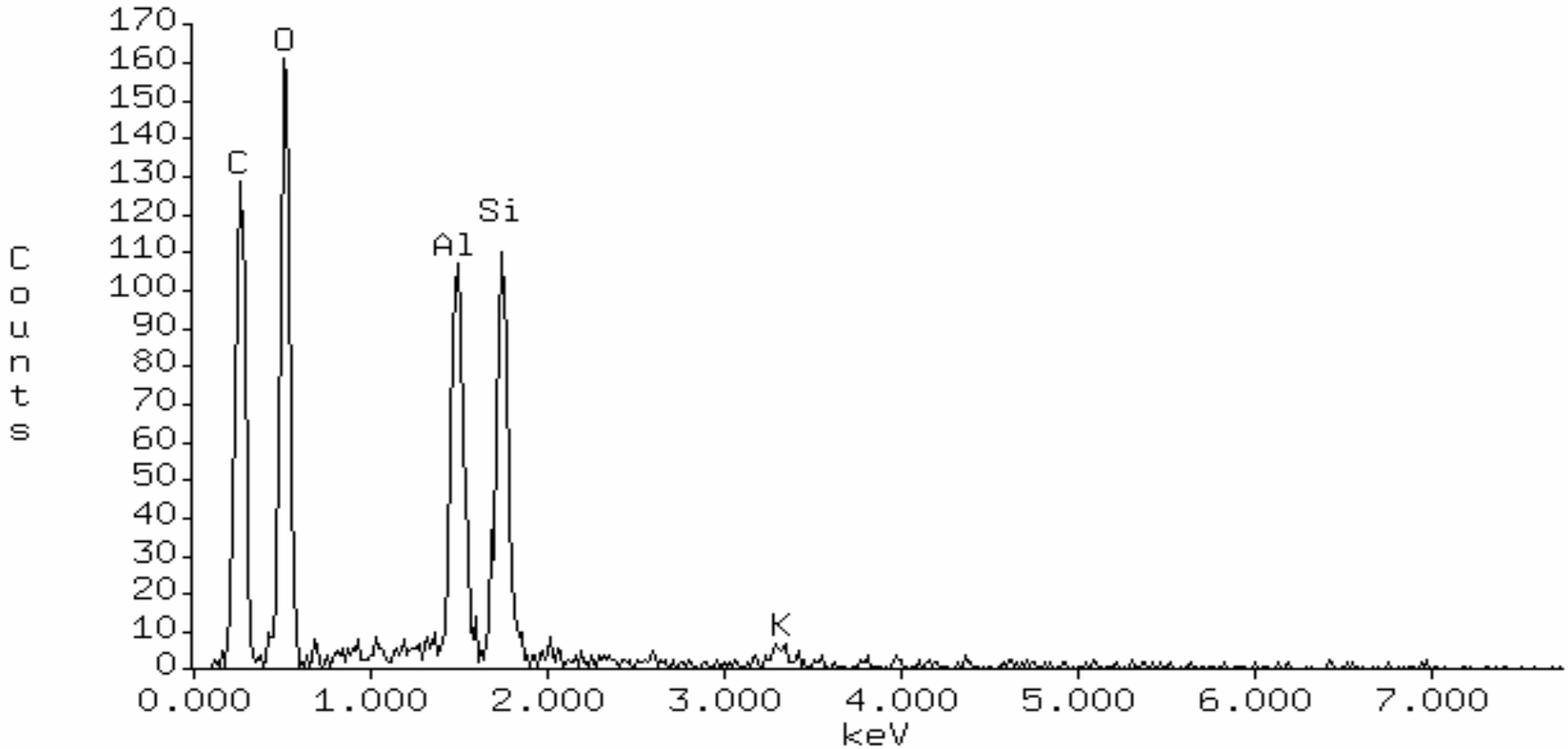
$$2\ KCl(g) + Al_2O_3 \cdot 2\ SiO_2(s) + H_2O(g) =$$

$$K_2O \cdot Al_2O_3 \cdot 2\ SiO_2(s) + 2\ HCl(g)$$

KCl(g) - Kaolin Reaction in Laboratory (TGA)

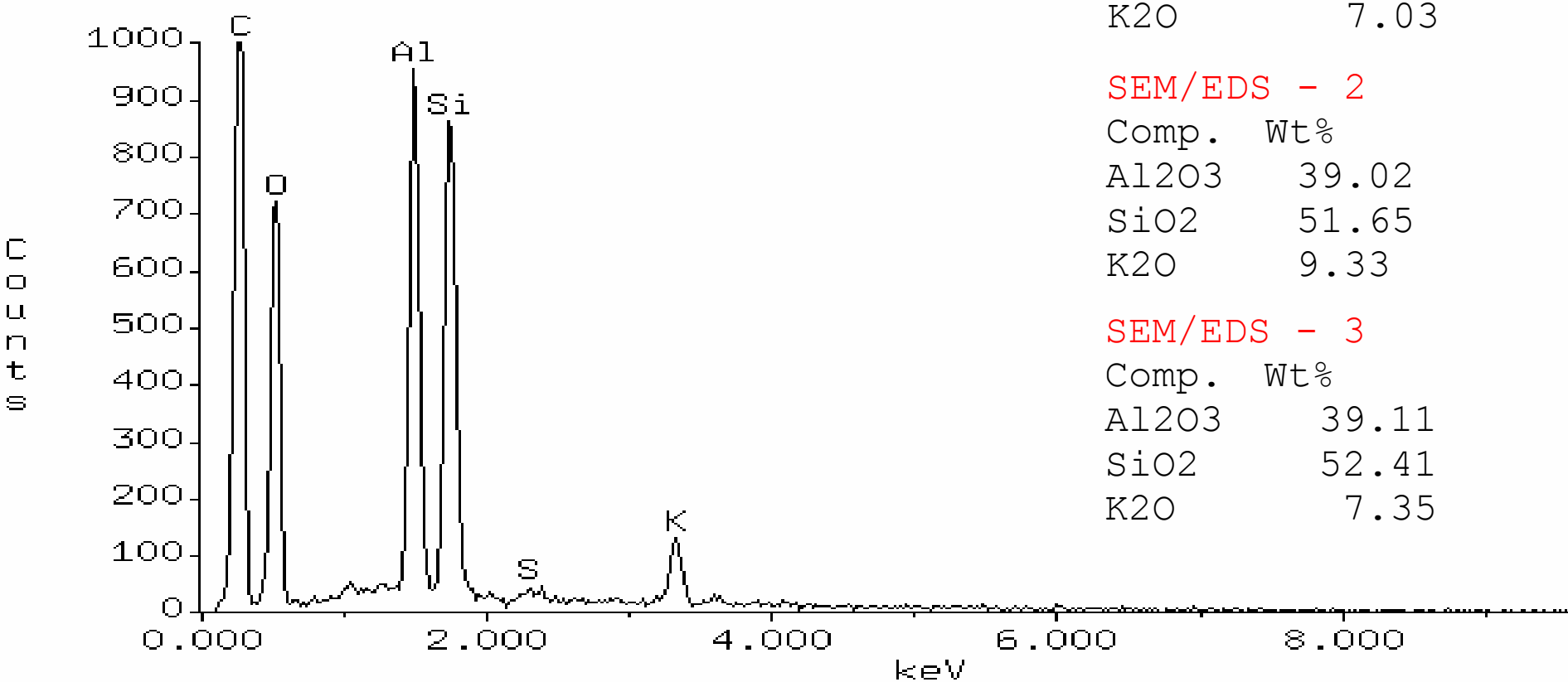


Kaolin Unreacted - EDX Analysis



Kaolin Reacted with KCl(g)

(Glazer et al 2007)



SEM/EDS - 1

Comp.	Wt%
Al2O3	37.31
SiO2	52.64
K2O	7.03

SEM/EDS - 2

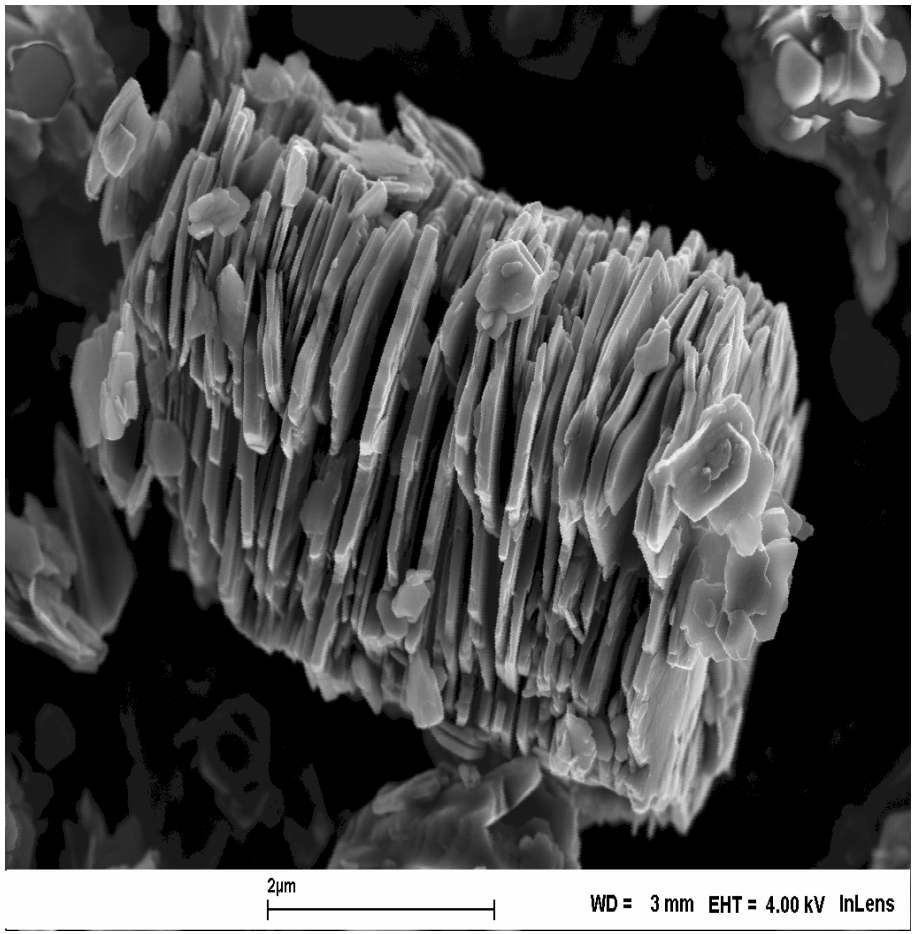
Comp.	Wt%
Al2O3	39.02
SiO2	51.65
K2O	9.33

SEM/EDS - 3

Comp.	Wt%
Al2O3	39.11
SiO2	52.41
K2O	7.35

Kaolin – SEM images

UNREACTED



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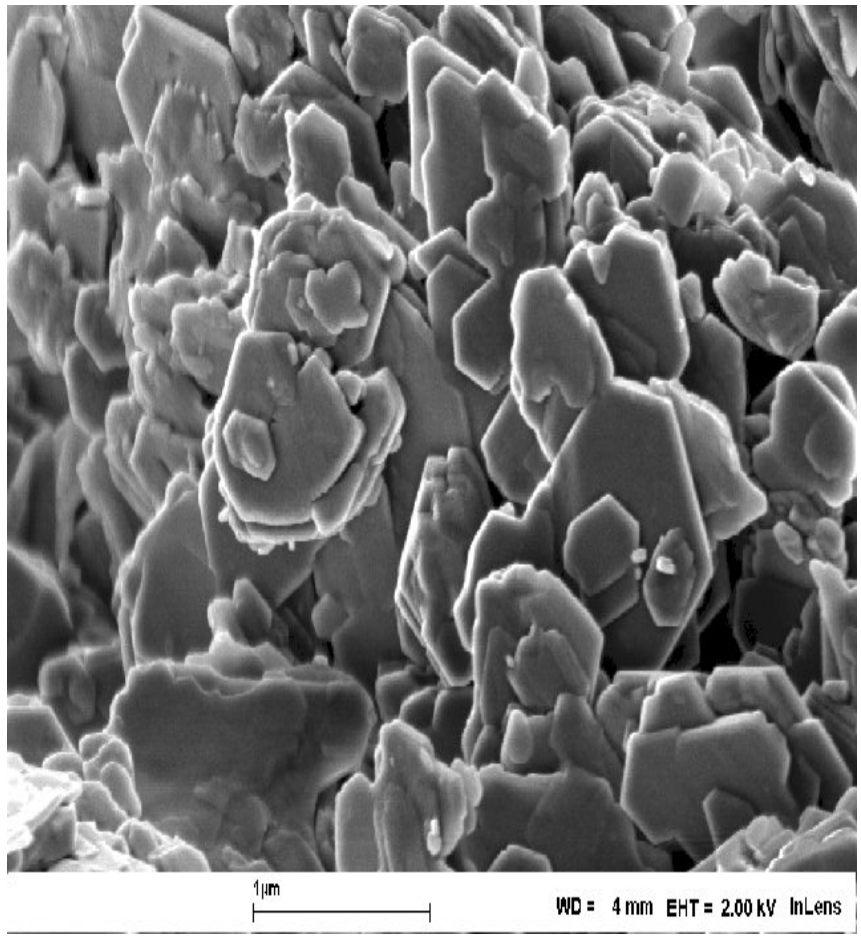

(Glazer et al. 2007)

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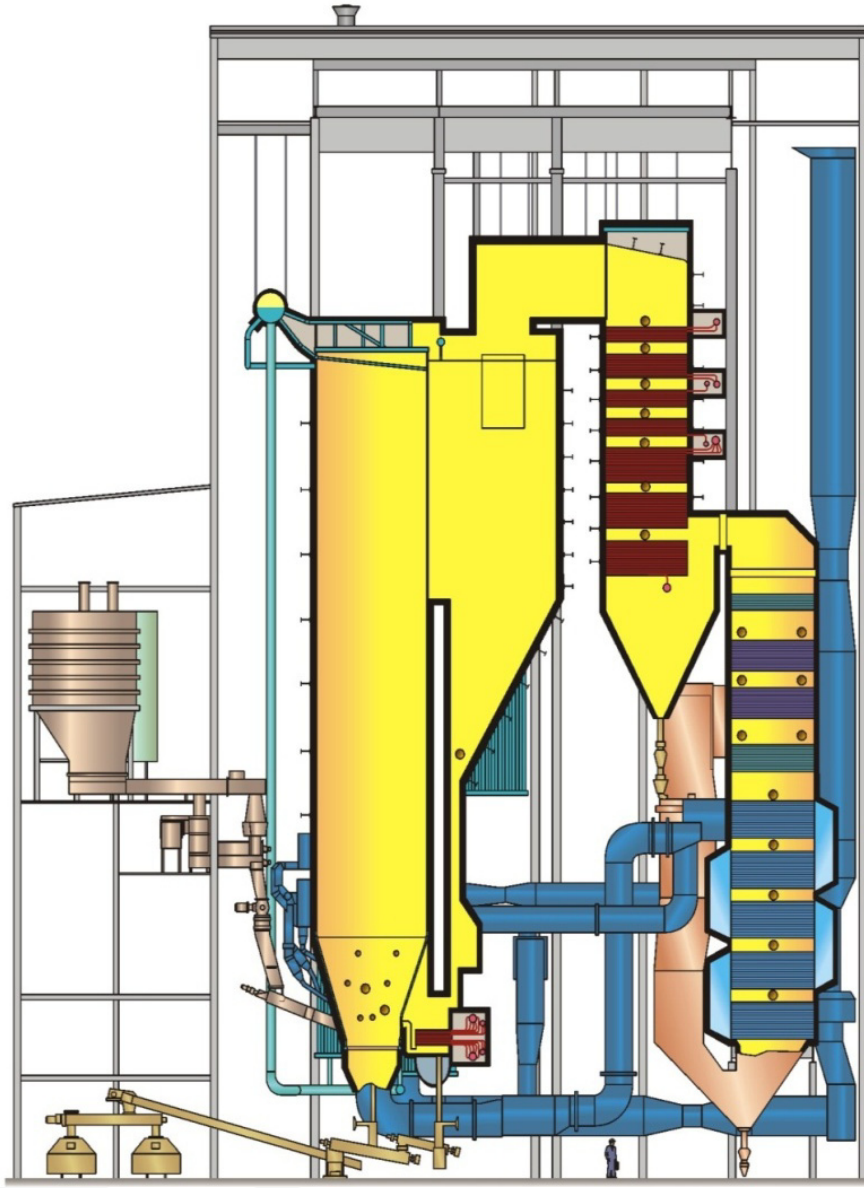
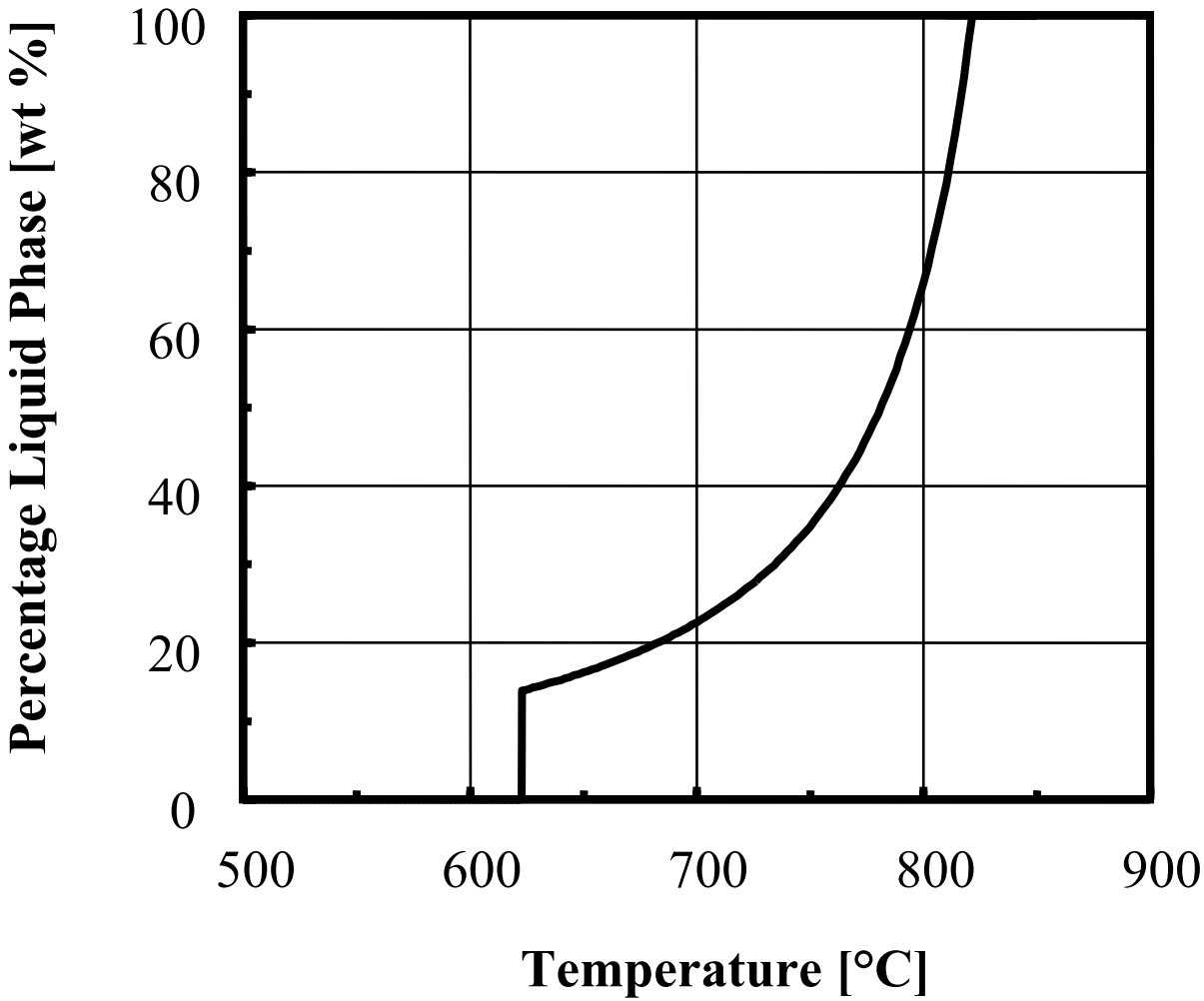
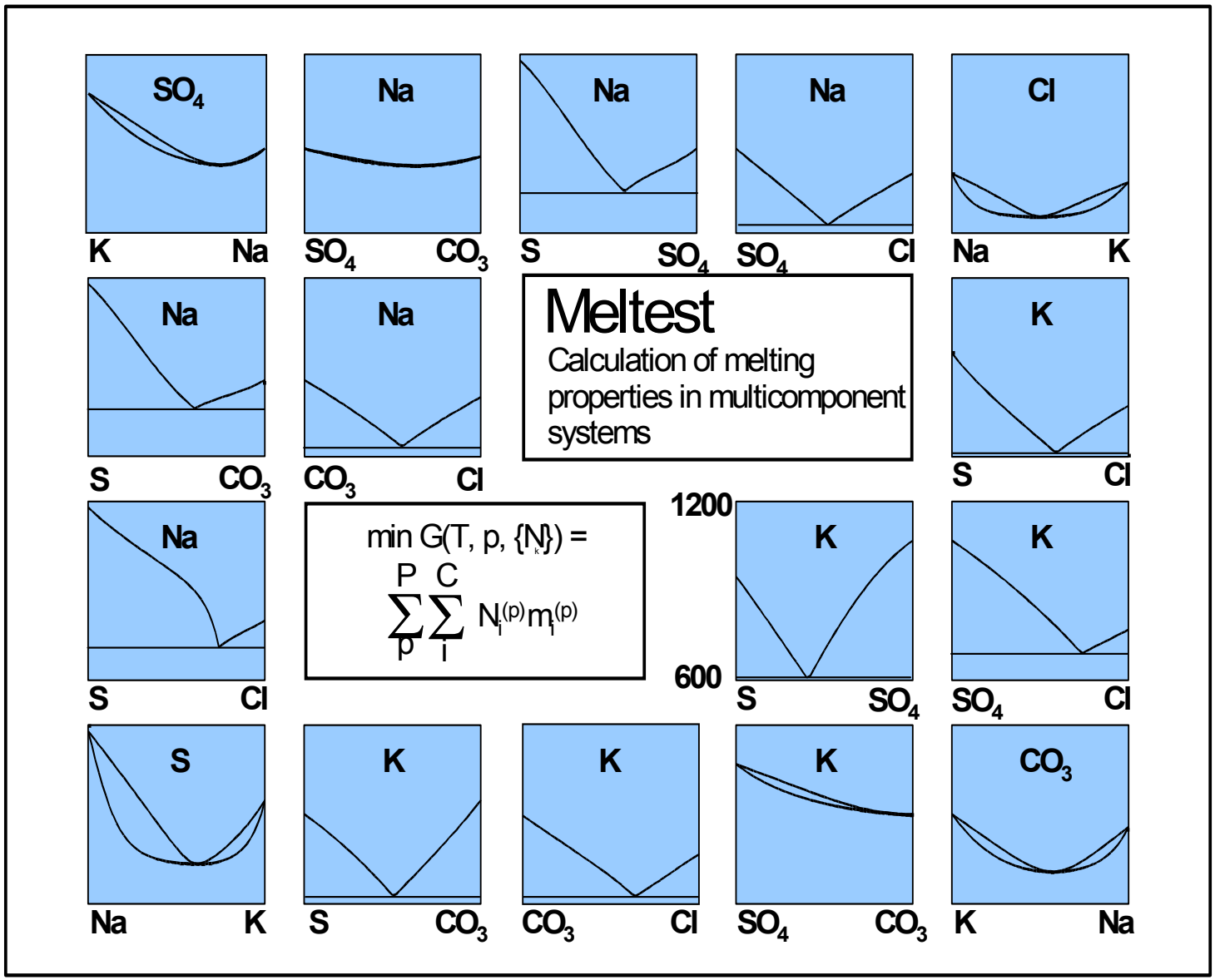


Figure courtesy: Mälarenergi Ab & Foster Wheeler

Percentage Molten Phase vs. Temperature

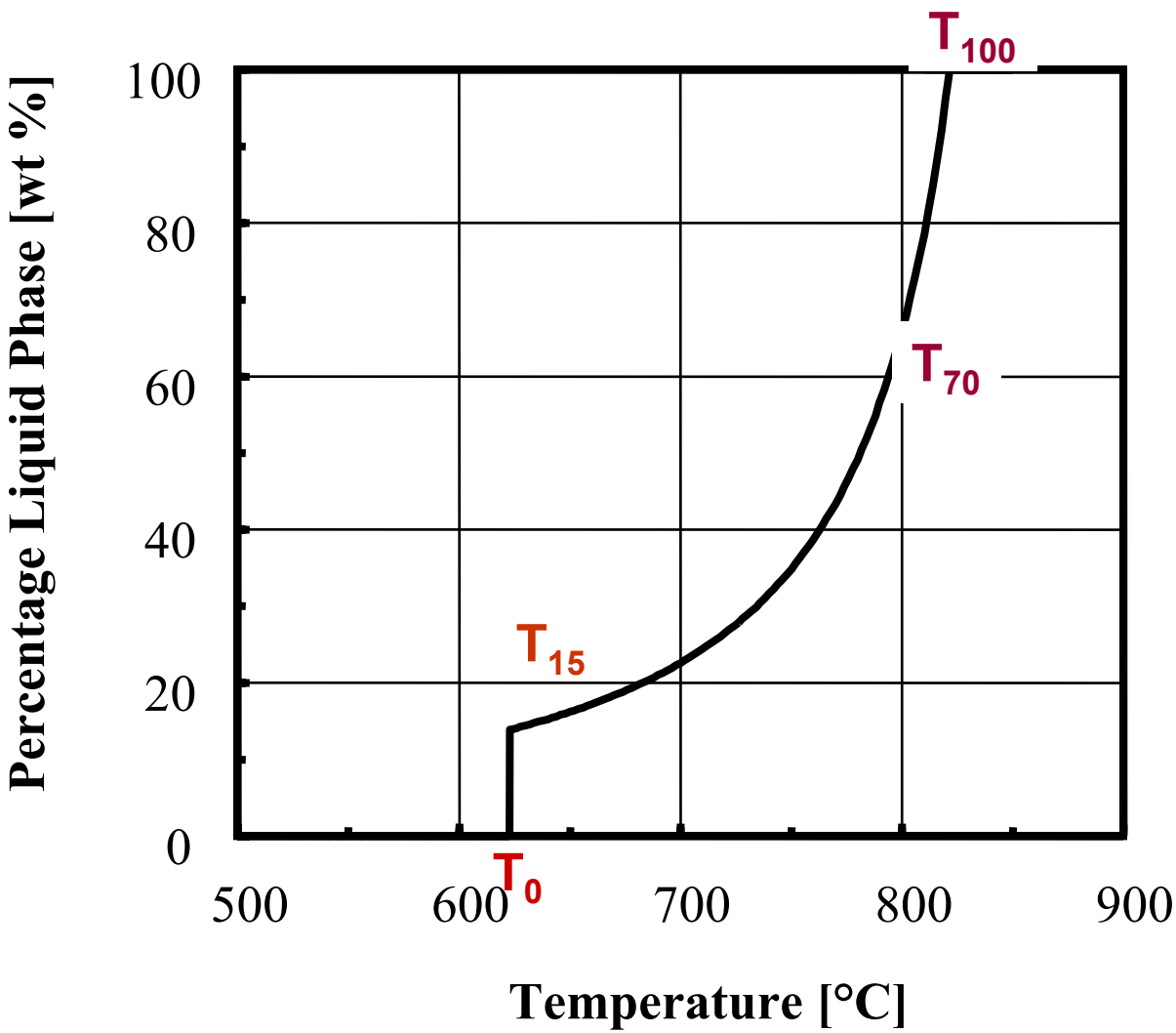


Alkali Salt Melting Property Predictor



(Backman et al. 1999)

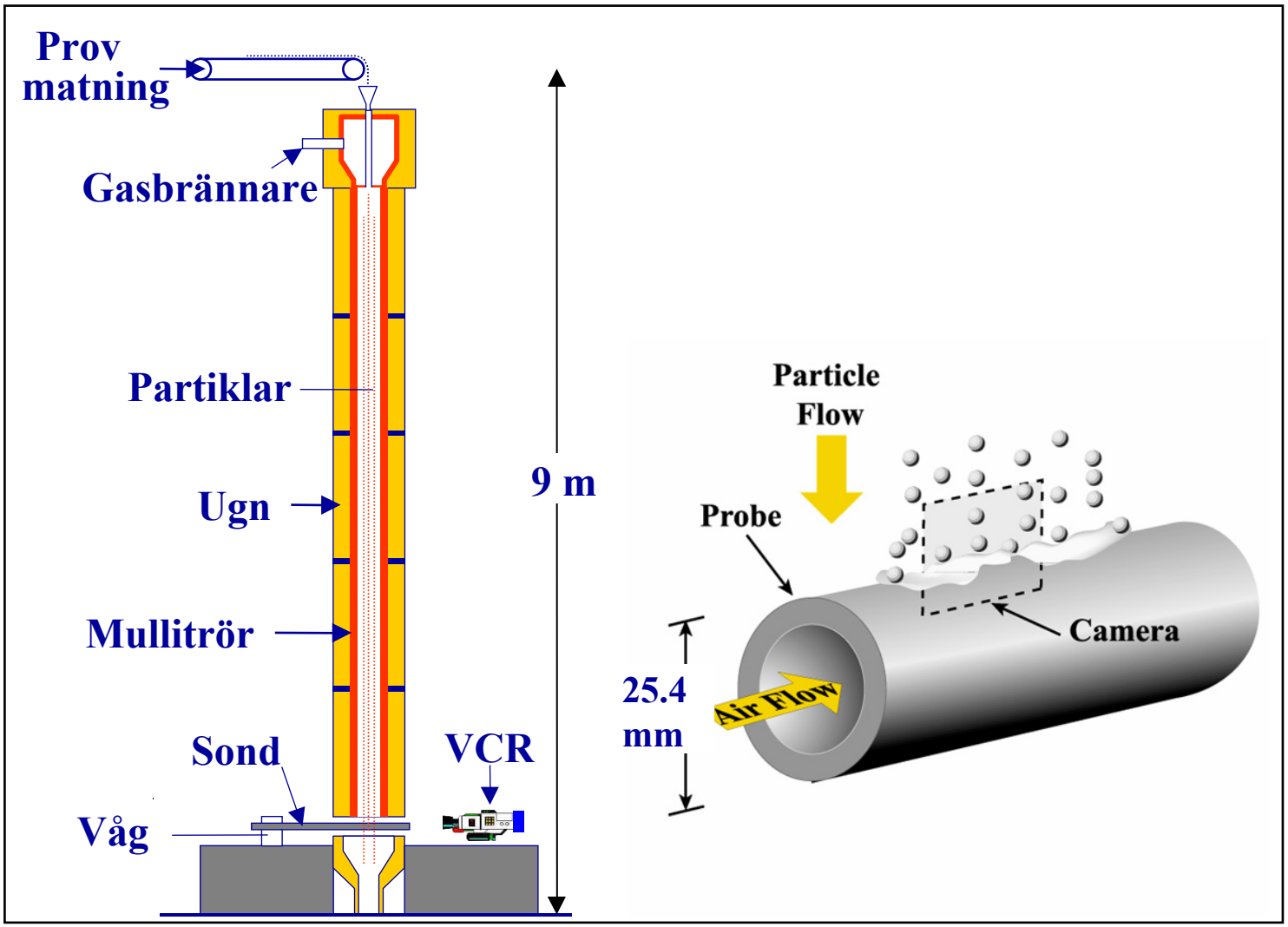
Percentage Molten Phase vs. Temperature & Characteristic Temperatures



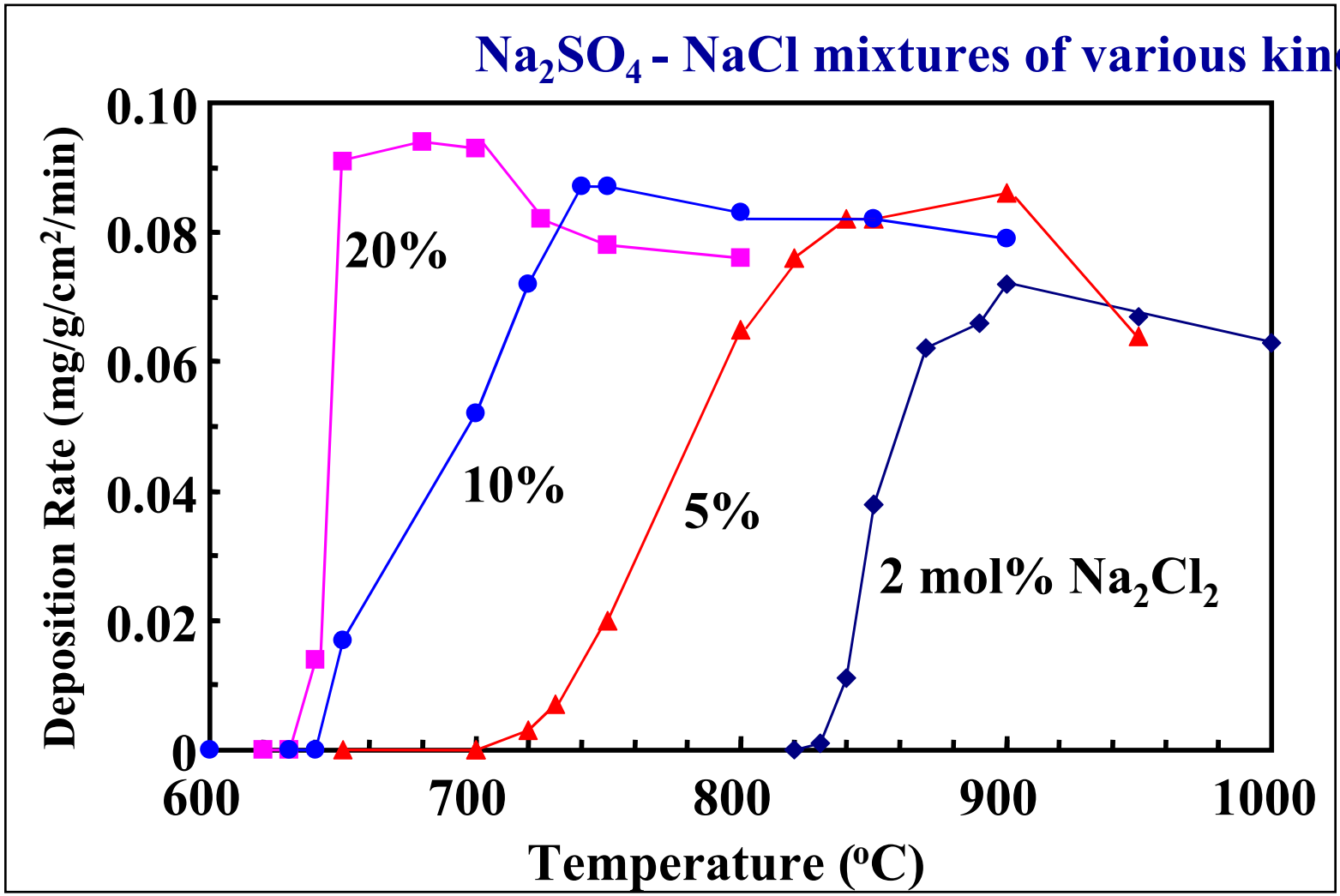
(Backman et al. 1987)

Entrained Flow Particle Reactor

University of Toronto



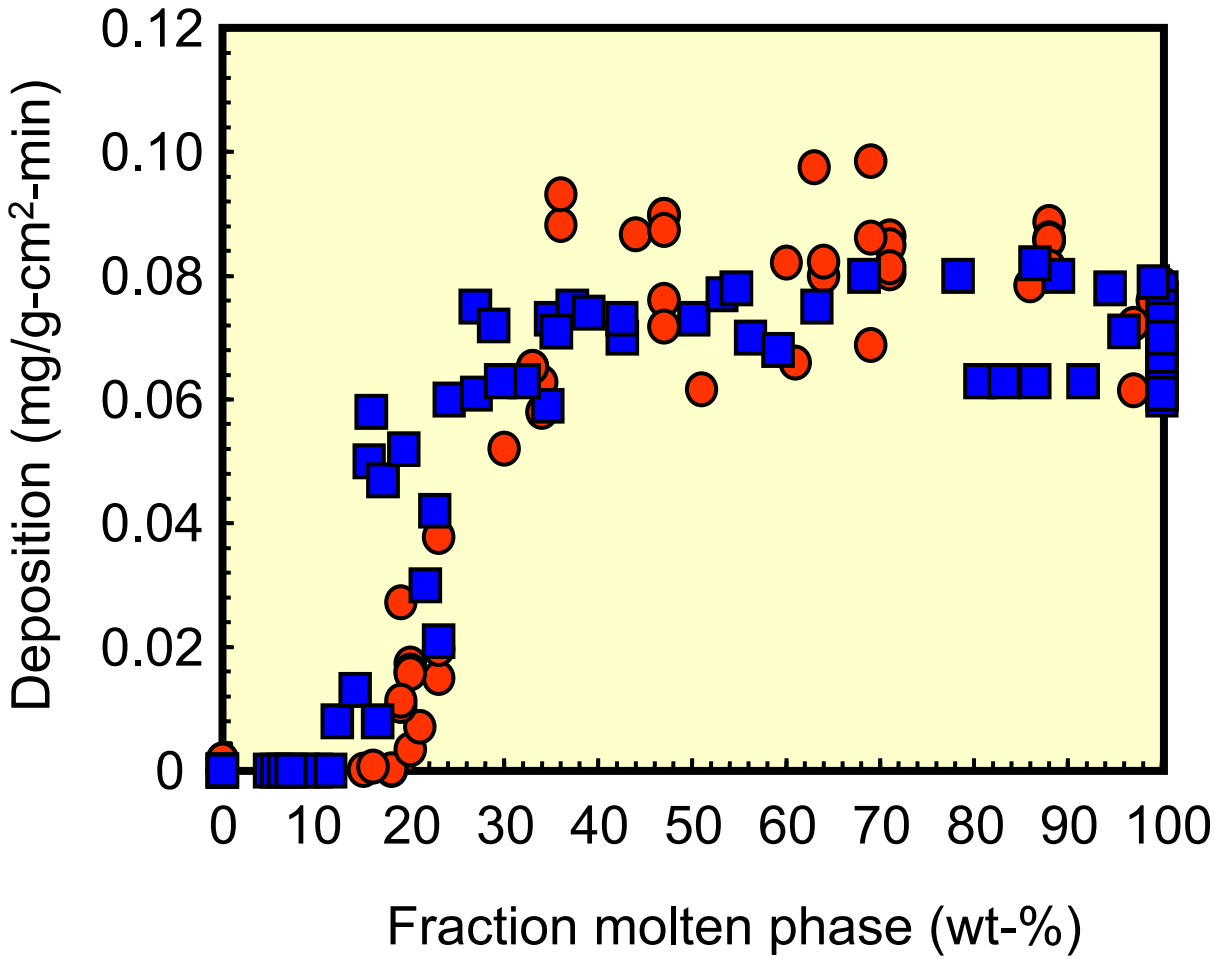
Stickiness of Salt Particles vs. Temperature and Composition



(Tran et al. 2002)

Stickiness of Partially Molten Particles

Entrained Flow Reactor Tests in Toronto



(Tran et al. 2002)

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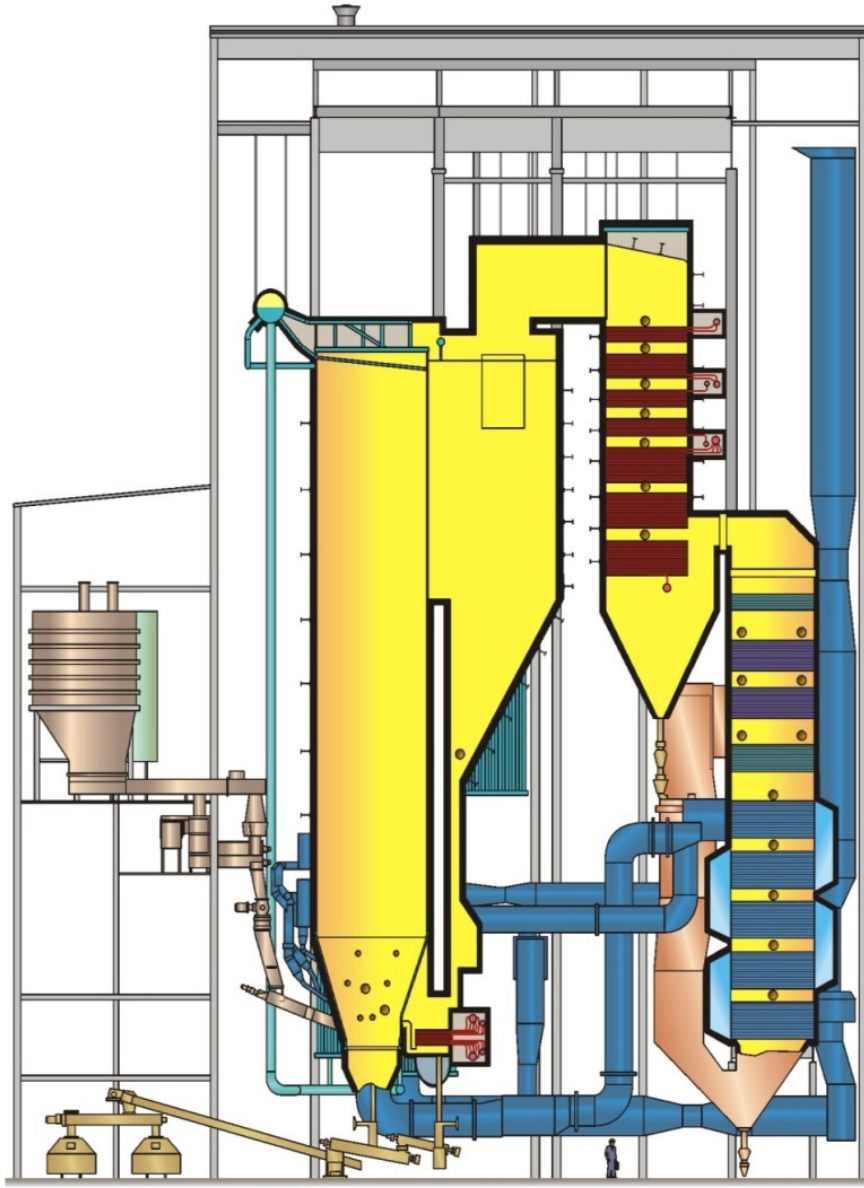
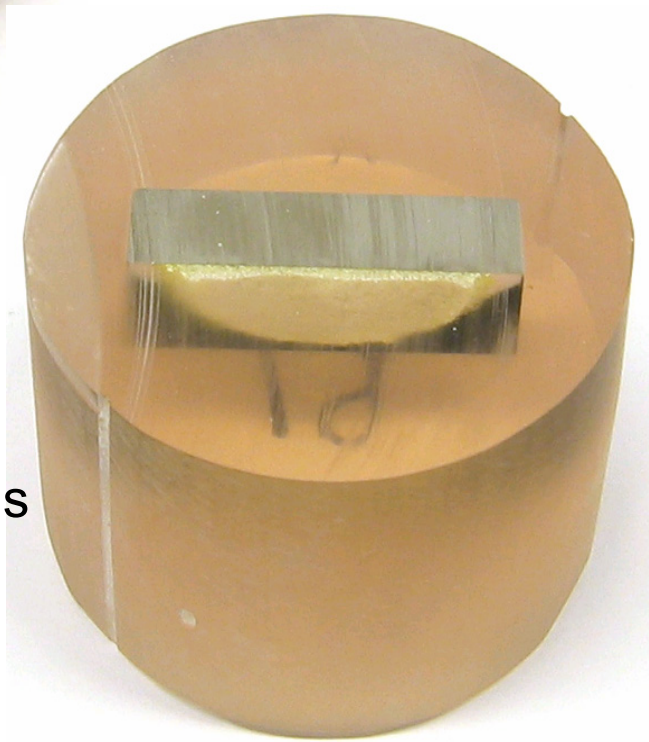


Figure courtesy: Mälarenergi Ab & Foster Wheeler

Test of Salt Induced Corrosion

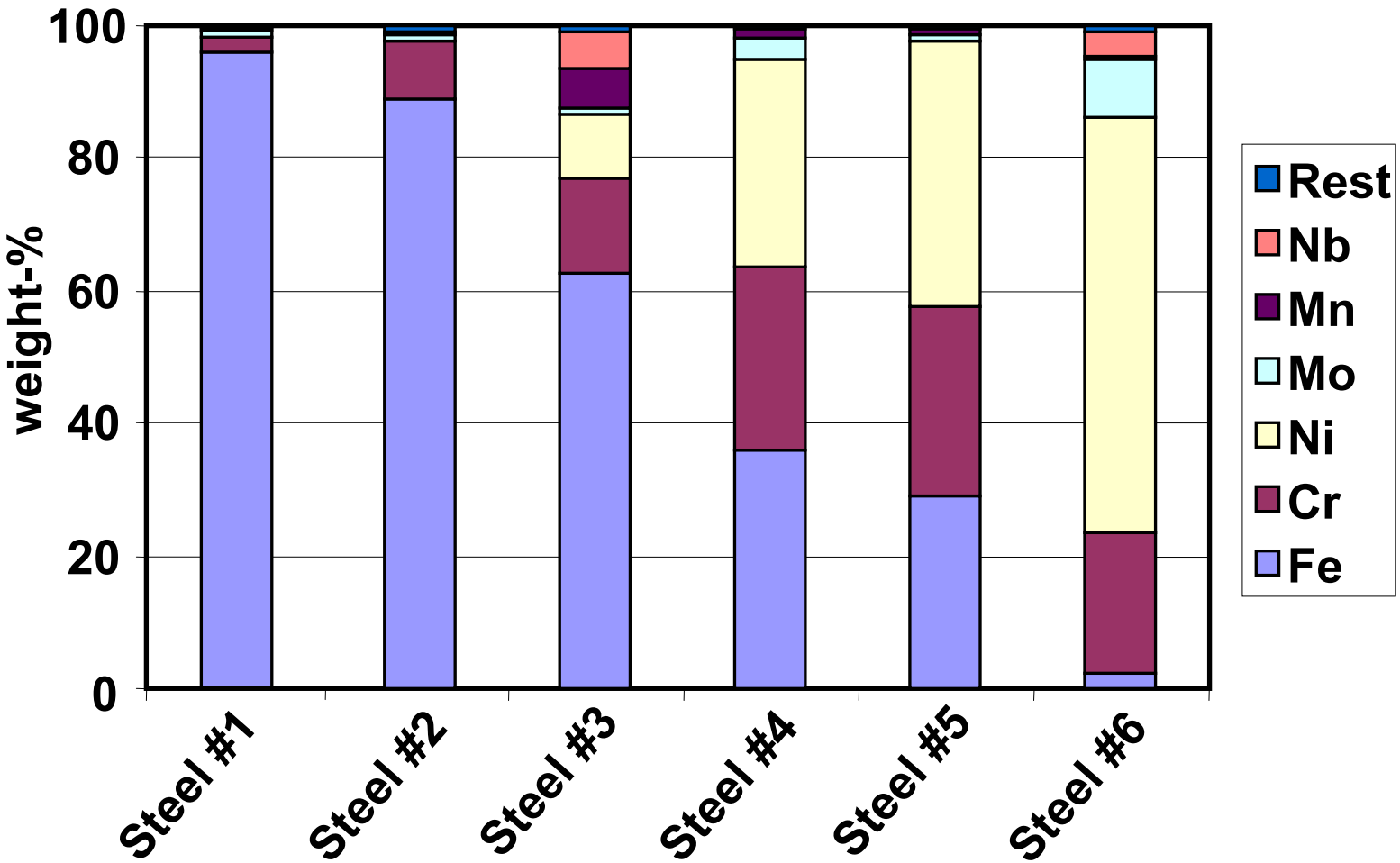
Specimen before heat treatment

Specimen after heat treatment



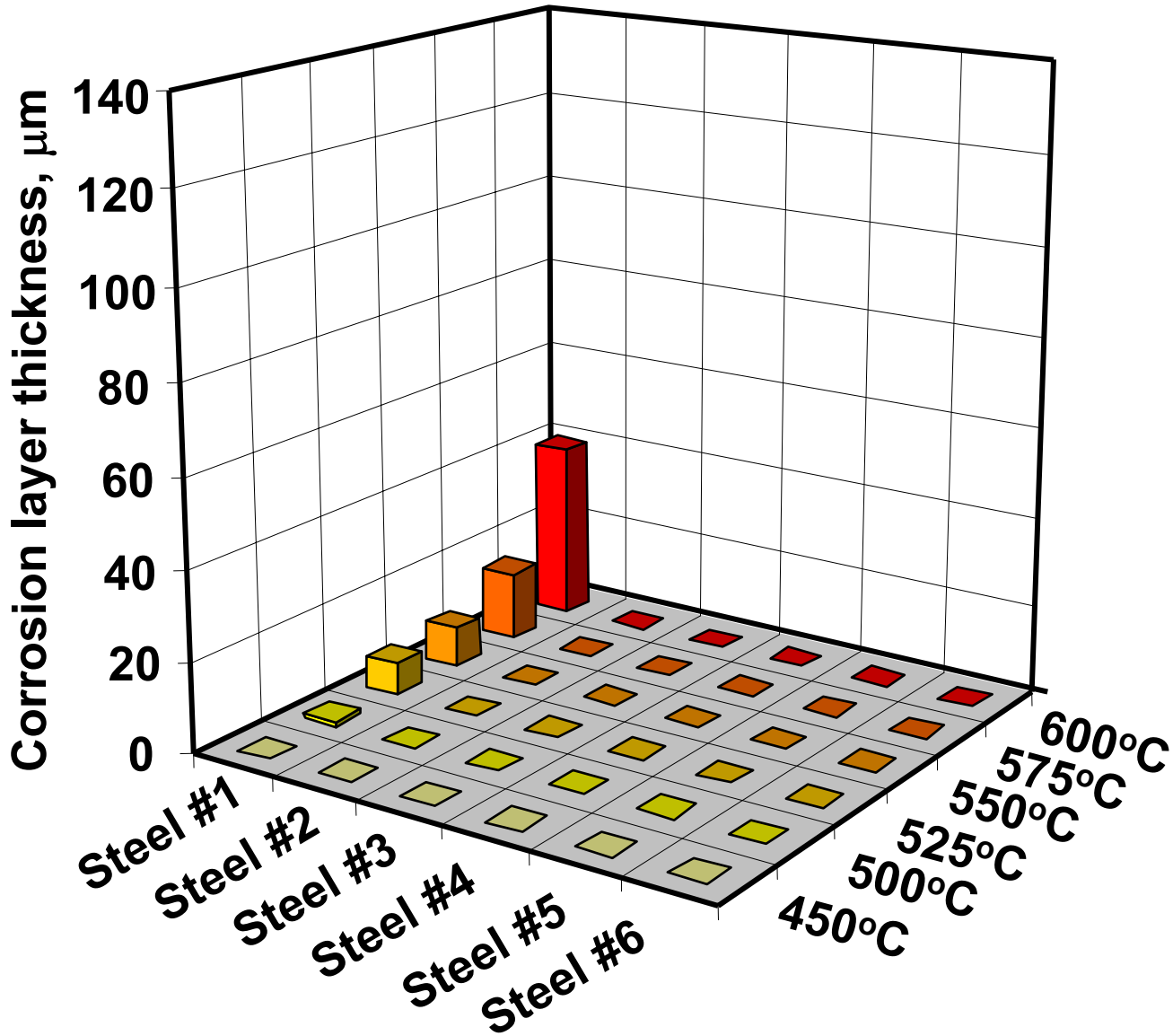
Cross-section for SEM analysis

The steels in the tests



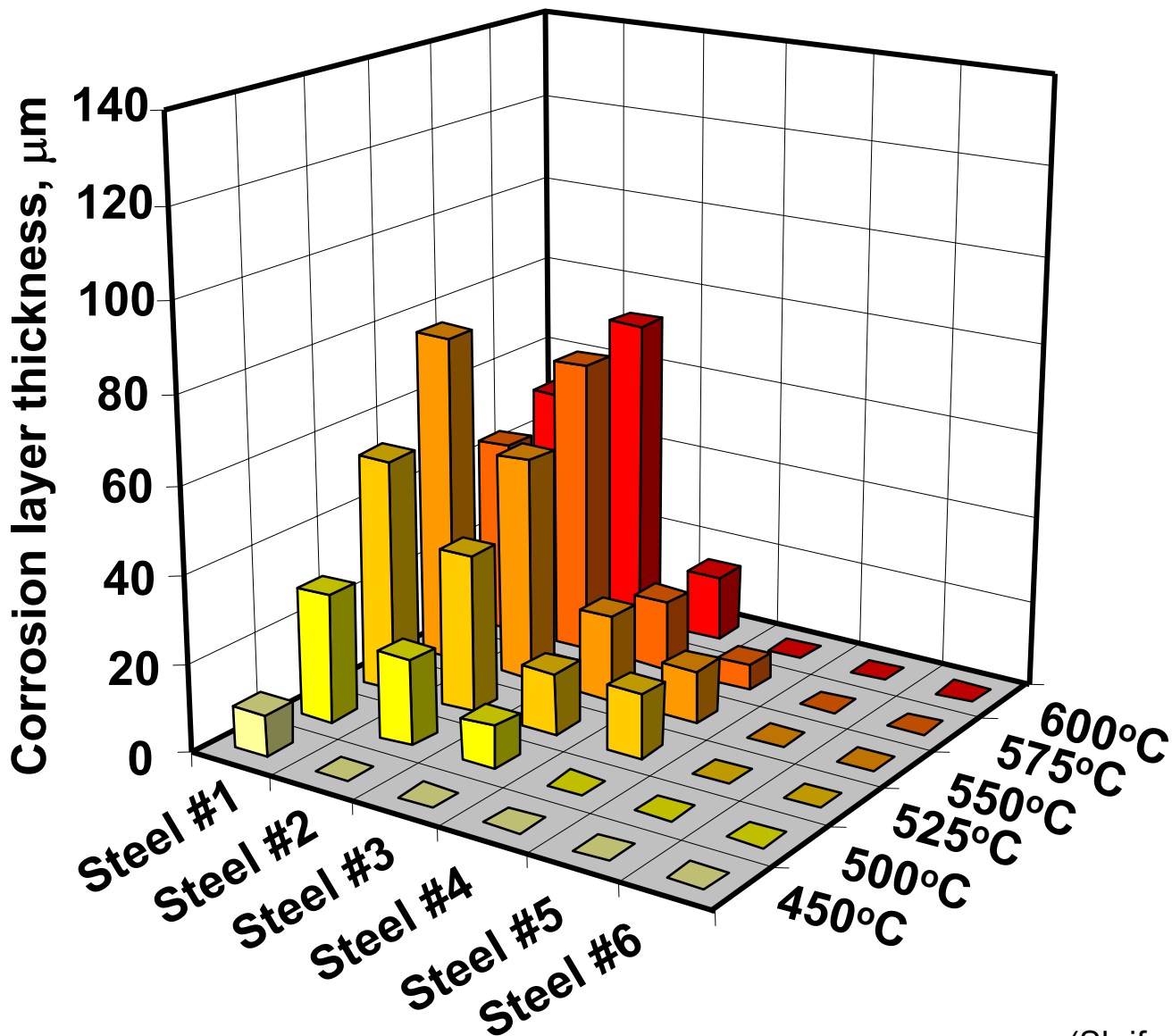
(Skrifvars et al. 2008)

$(Na,K)_2SO_4$ + 0% Cl



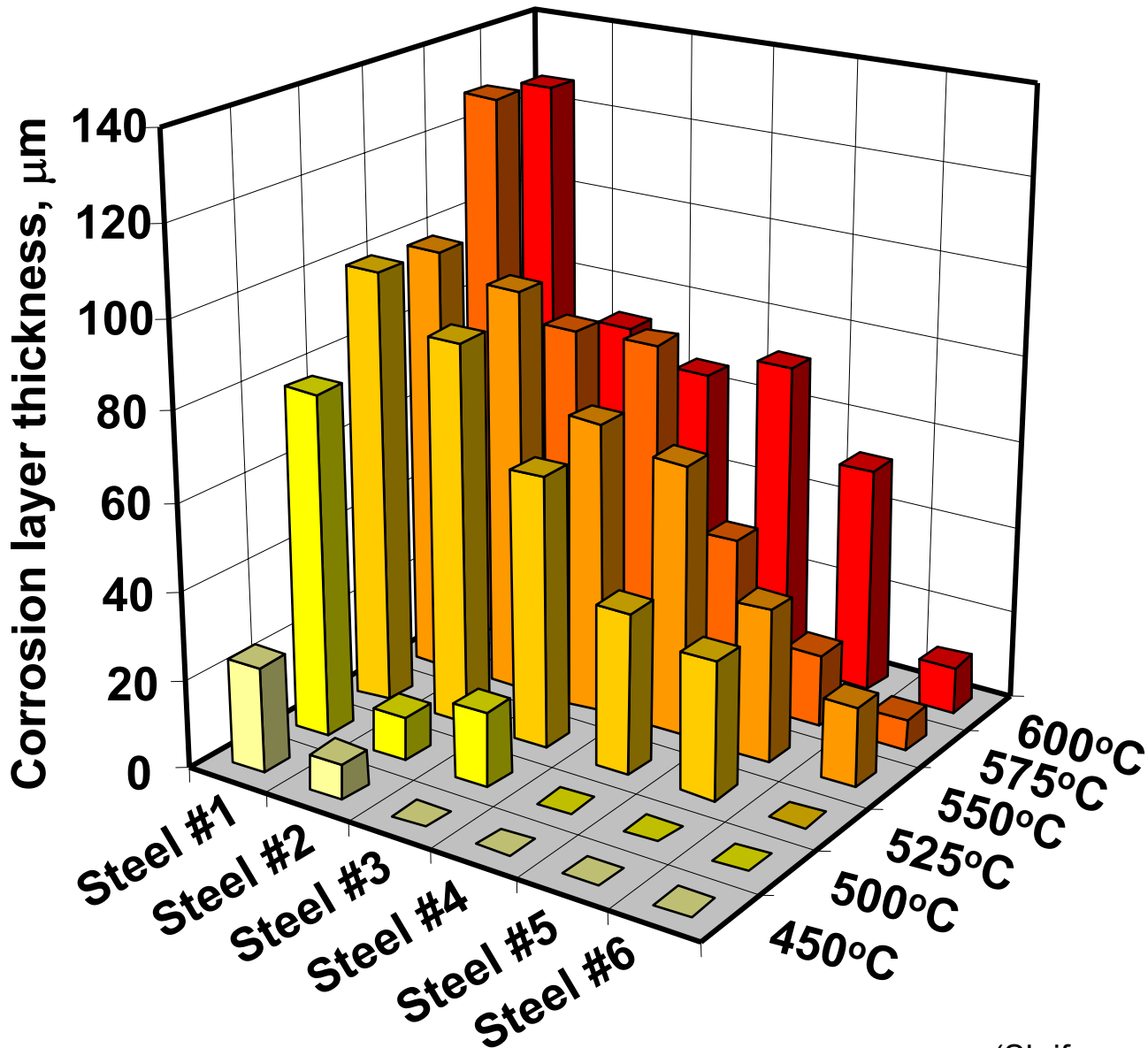
(Skrifvars et al. 2008)

$(Na,K)_2SO_4$ + 0.3% Cl



(Skrifvars et al. 2008)

$(Na,K)_2SO_4$ + 1.3% Cl



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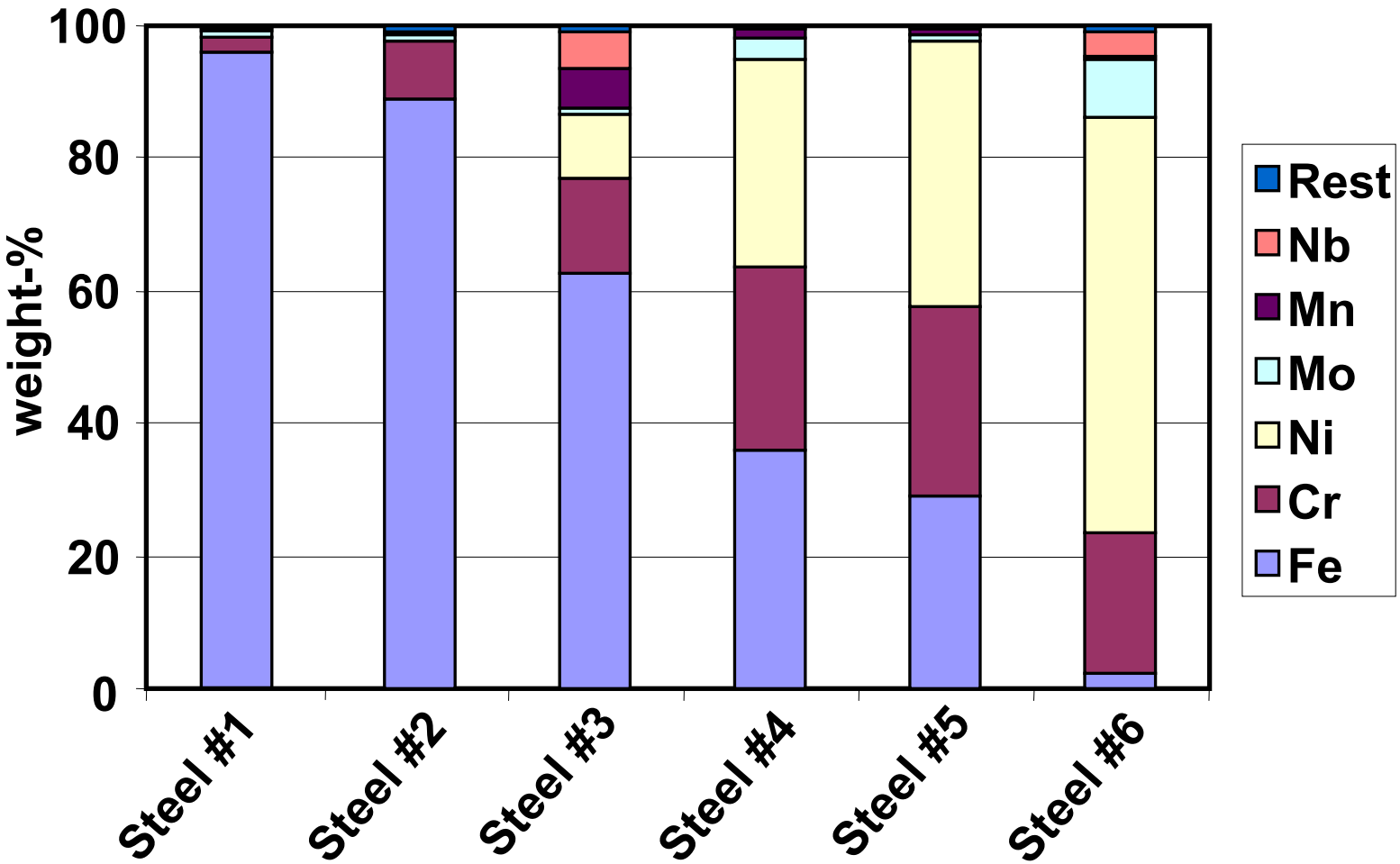

Price/kg (x St 45.8)	1,8	10	26	53

Conclusions (1)

- Ash related problems major risk with biomass or waste derived fuels in FBC
- Understanding of ash behavior strongly improved
- Thermodynamic models helpful for understanding main ash chemistry
- Release/reactivity of ash forming matter not well understood – better characterization methods needed

Conclusions (2)

- Fouling connected with fly ash ash melting – melting prediction well advanced
- Corrosion mechanisms controversial – better insight may lead to new solutions
- Alternative bed materials interesting: reactive or inert
- Fuel mixtures major challenge for research

Aknowledgements

Bo Leckner
Kim Dam-Johansen
Johan Hustad
Flemming Frandsen
Honghi Tran
Rainer Backman
Benco Skrifvars
Patrik Yrjas
Maria Zevenhoven
Christian Mueller
Anders Brink
Johan Werkelin
Mischa Theis
Daniel Lindberg
Jatta Partanen
Vesna Barisic
Edgardo Coda Zabetta.

Andritz Oy
Foster Wheeler Energia Oy
Metso Power Oy,
Oy Metsä-Botnia Ab
Vattenfall Utveckling AB
International Paper.

Tekes

Academy of Finland