Experiences with waste wood/sludge co-firing in Sweden

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Financial support from the
Swedish Energy Agency

Energimyndigheten

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The story in short

1) Waste wood is contaminated with Zn and Cl

    => increased problems with deposits

2) The deposit formation can be radically decreased by co-combustion with sewage sludge
3) What are the underlying mechanisms?

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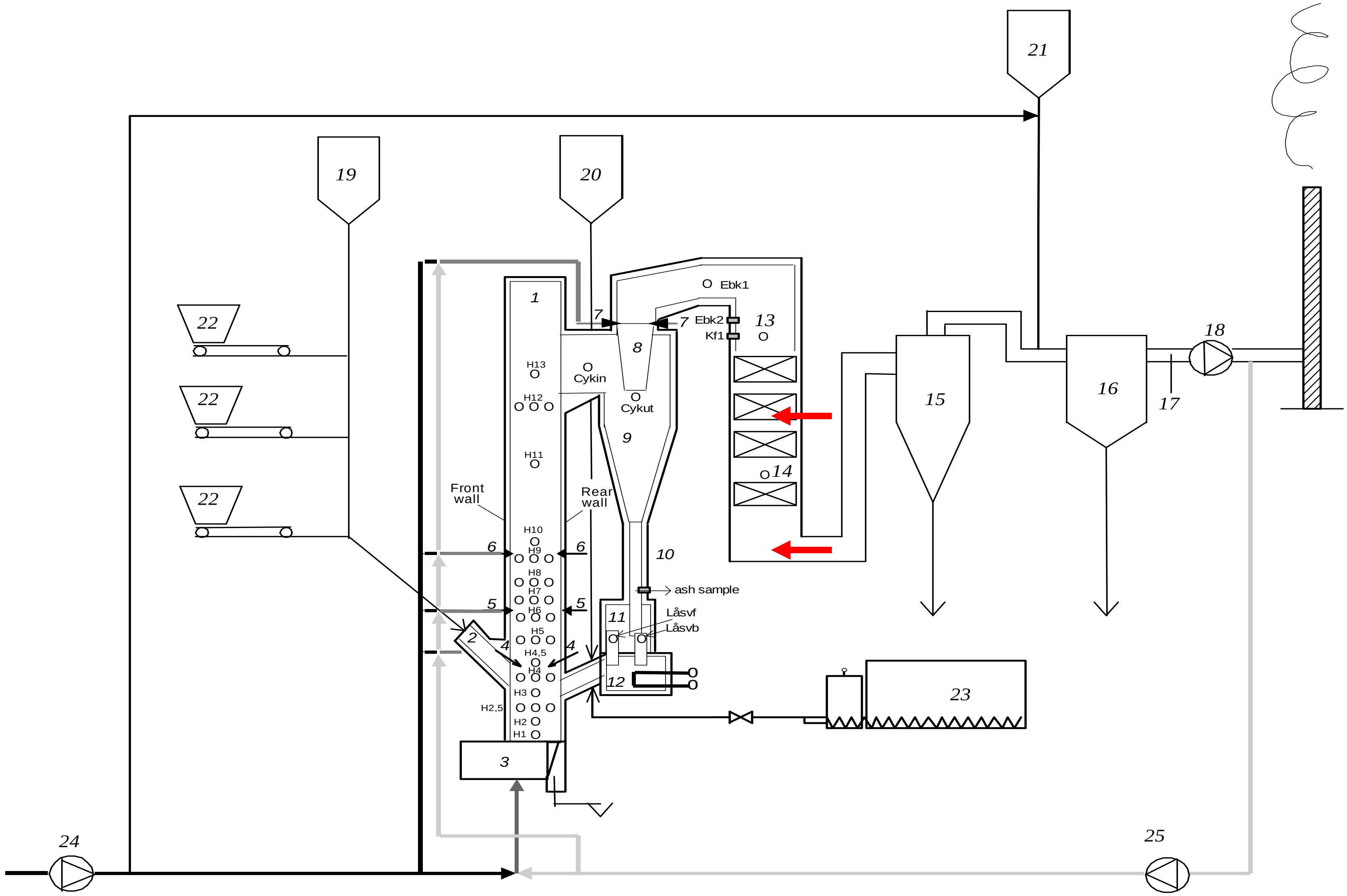
Experiments have been performed in Chalmers 12 MW CFB



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Experimental - Fuels

- Wood pellets
- Waste wood
- Sewage sludge

Three different waste wood qualities were simulated:

1) “Clean” waste wood
2) “Normally” contaminated waste wood: Added ZnO (pigment in old paint)
3) Painted waste wood with high chlorine content: Added ZnO and HCl

Fuel Analysis

	Wood pellets	Waste wood	Sewage sludge
Proximate analysis			
Moisture (mass %, raw)	8.6	33.1	72.8
Ash (mass %, dry)	0.6	0.8	46.9
Ultimate analysis (mass %, daf)			
C	50.3	50.0	51.7
H	6.1	6.1	7.2
O	43.5	43.7	32.9
S	0.01	0.01	1.8
N	0.09	0.17	6.2
Cl	0.01	0.02	0.1
Heating value (MJ/kg daf)	18.6	18.0	20.5
Ash analysis (g/kg dry ash)			
K	87	70	13
Na	5.9	26	7.8
Al	11	14	73
Si	64	65	130
Fe	16	57	170
Ca	190	152	42
Mg	33	26	10
P	13	7.2	66

Test programme

WP: Wood Pellets

MS: Municipal Sewage sludge

Number: mass dry fuel / mass total dry fuel)%)

(balance = waste wood)

Runs	Molar ratio Cl/Zn	S/Zn	Cl / (K+Na)	2S / (K+Na)	2S/Cl
WP38	4.4	6.0	0.11	0.3	2.7
WP33+MS13	3.0	18	0.08	1.02	12.8
WP56+ZnO	0.91	0.64	0.27	0.4	1.5
WP48+ZnO+MS5	0.88	3.2	0.16	1.2	7.5
WP47+ZnO+MS9	0.97	5.9	0.16	1.9	11.9
WP51+ZnO+HCl	4.0	0.63	1.9	0.6	0.3
WP44+ZnO+HCl+MS6	3.9	3.8	0.80	1.6	2.0
WP43+ZnO+HCl+MS10	3.5	5.9	0.51	1.7	3.4

Experimental - Measurements

The particle size distribution of the fly ash in the convection pass has been measured:

- Number size distribution: ELPI
- Mass size distribution: DLPI and pre-cyclones

A simulated super heater probe (500 ^{o}C) has been used to collect and study the deposit formation in the super heater region

The samples from the DLPI and from the simulated super heater have been analysed chemically

Experimental - Chemical analysis

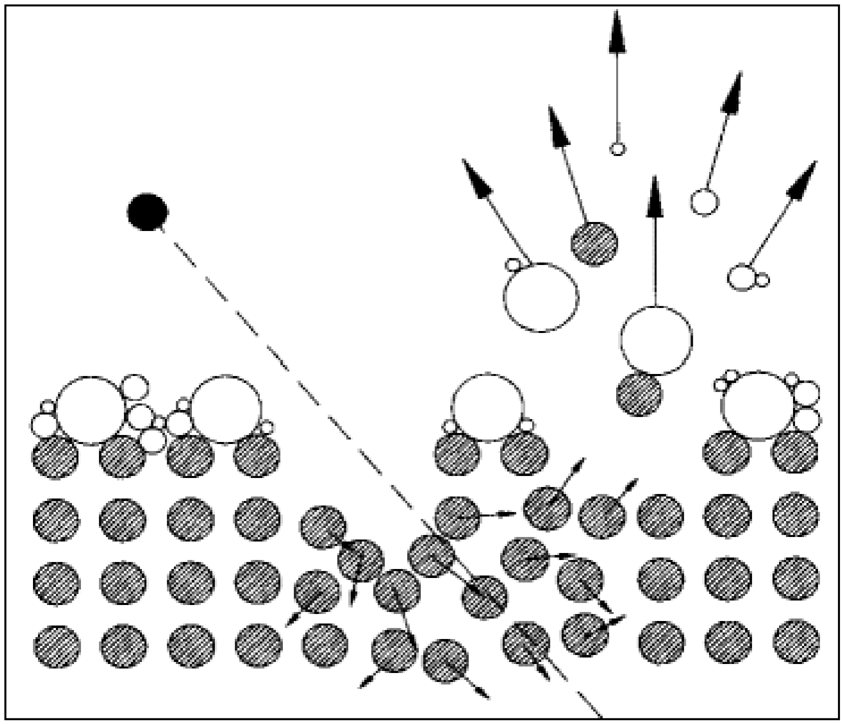
Some of the collected particle fractions have been characterized by using chemical analysis:

- The elemental concentrations have been analysed by ICP- OES, ICP- MS and ion chromatography (27 different elements)
- Different critical compounds have been analysed using TOF-SIMS (NaCl, KCl, K_2SO_4, K_2CO_3, $CaSO_4$ $Ca_3(PO_4)2$, ZnO, $ZnCl_2$ and $ZnSO_4$)

All deposit samples have been analysed as following:

1) Surface analysis on the wind side using TOF-SIMS
2) Elemental concentration of the complete deposit

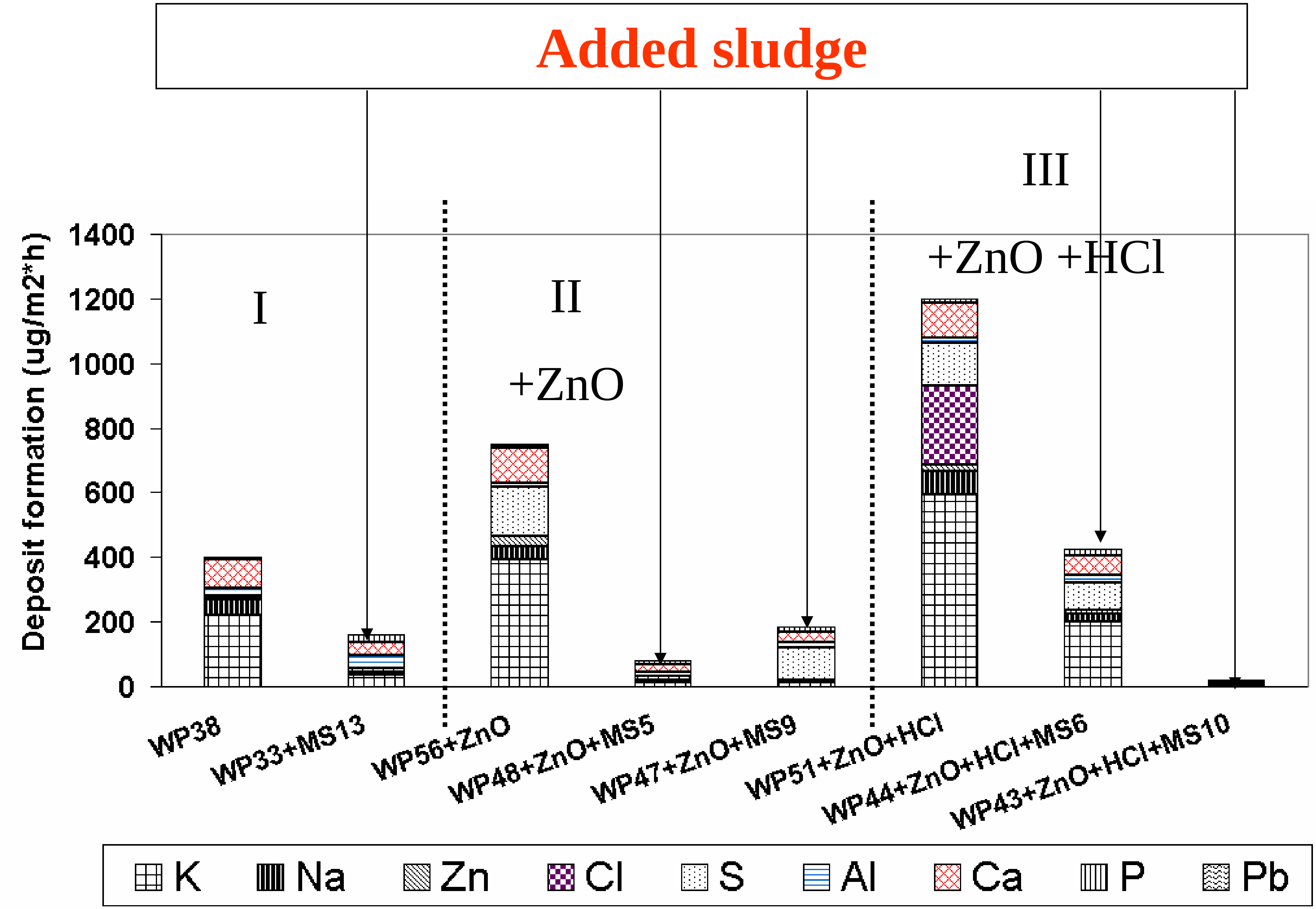
TOF-SIMS - Time-of-Flight Secondary Ion Mass Spectrometry



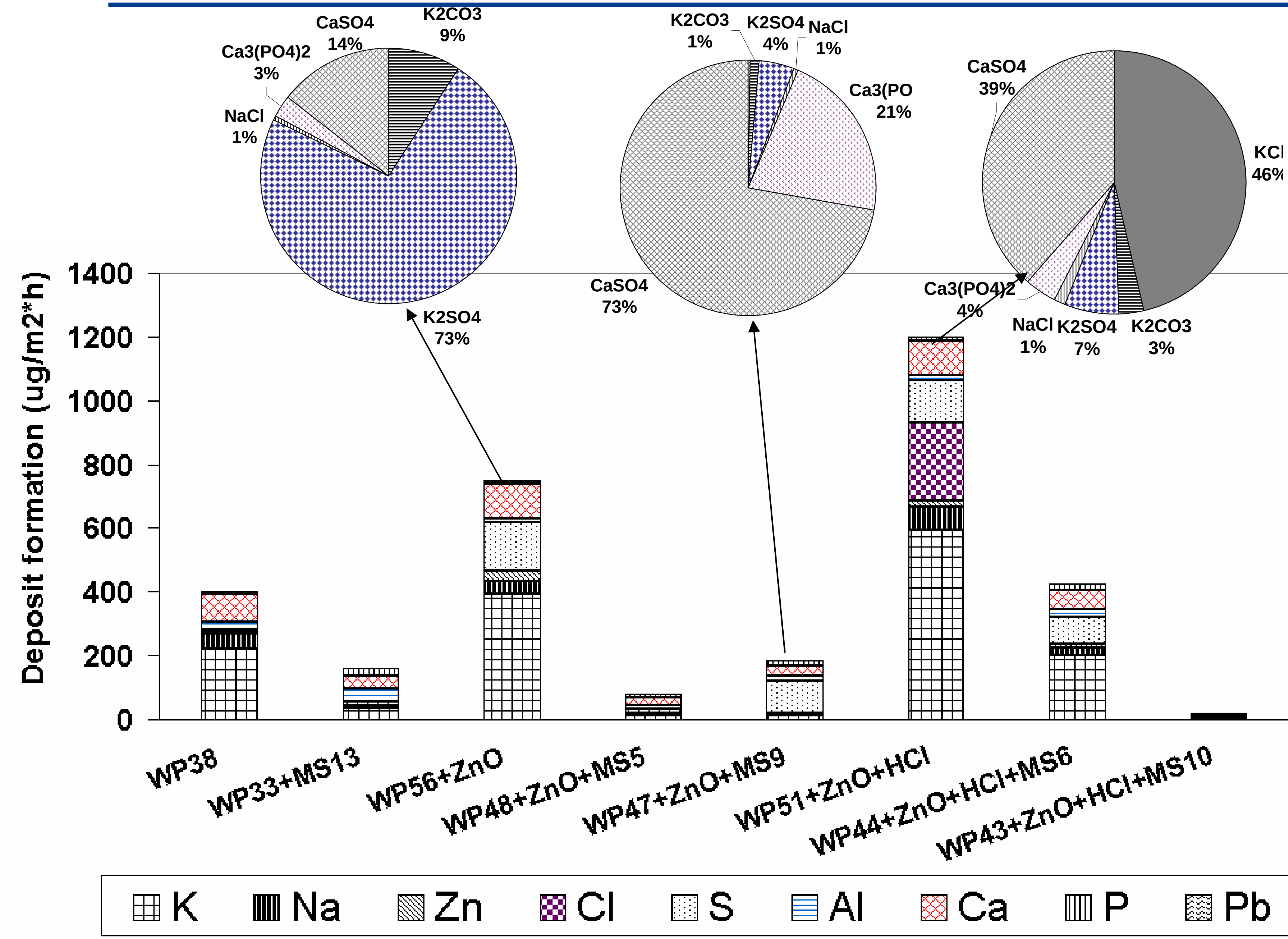
Schematic picture of the SIMS process.

A high energy ion hits the surface and gives rise to a cascade of secondary ions from the outermost 1-2 atomic layers of the sample surface. The secondary ions are detected by a mass spectrometer.

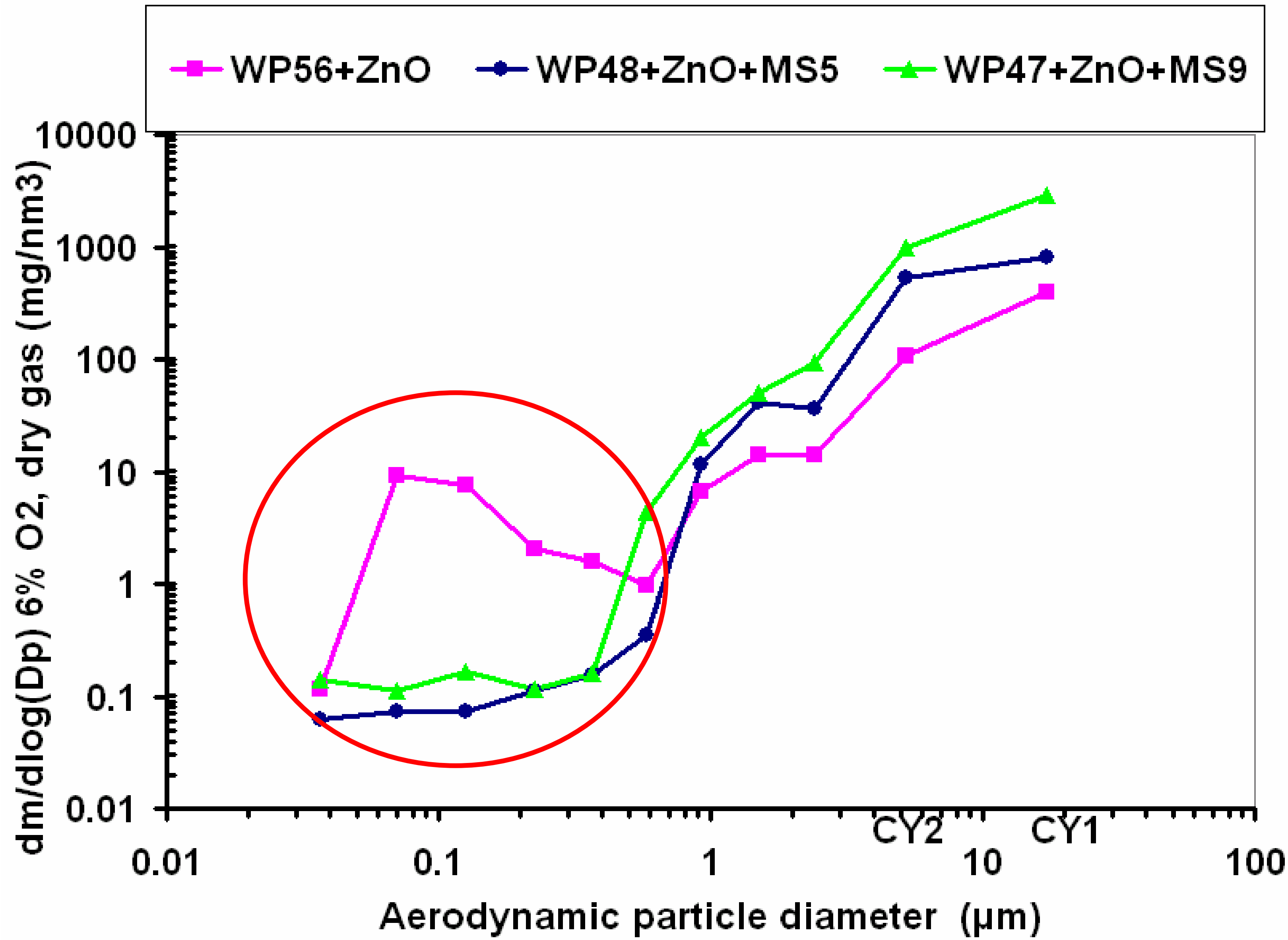
Results – Deposit formation



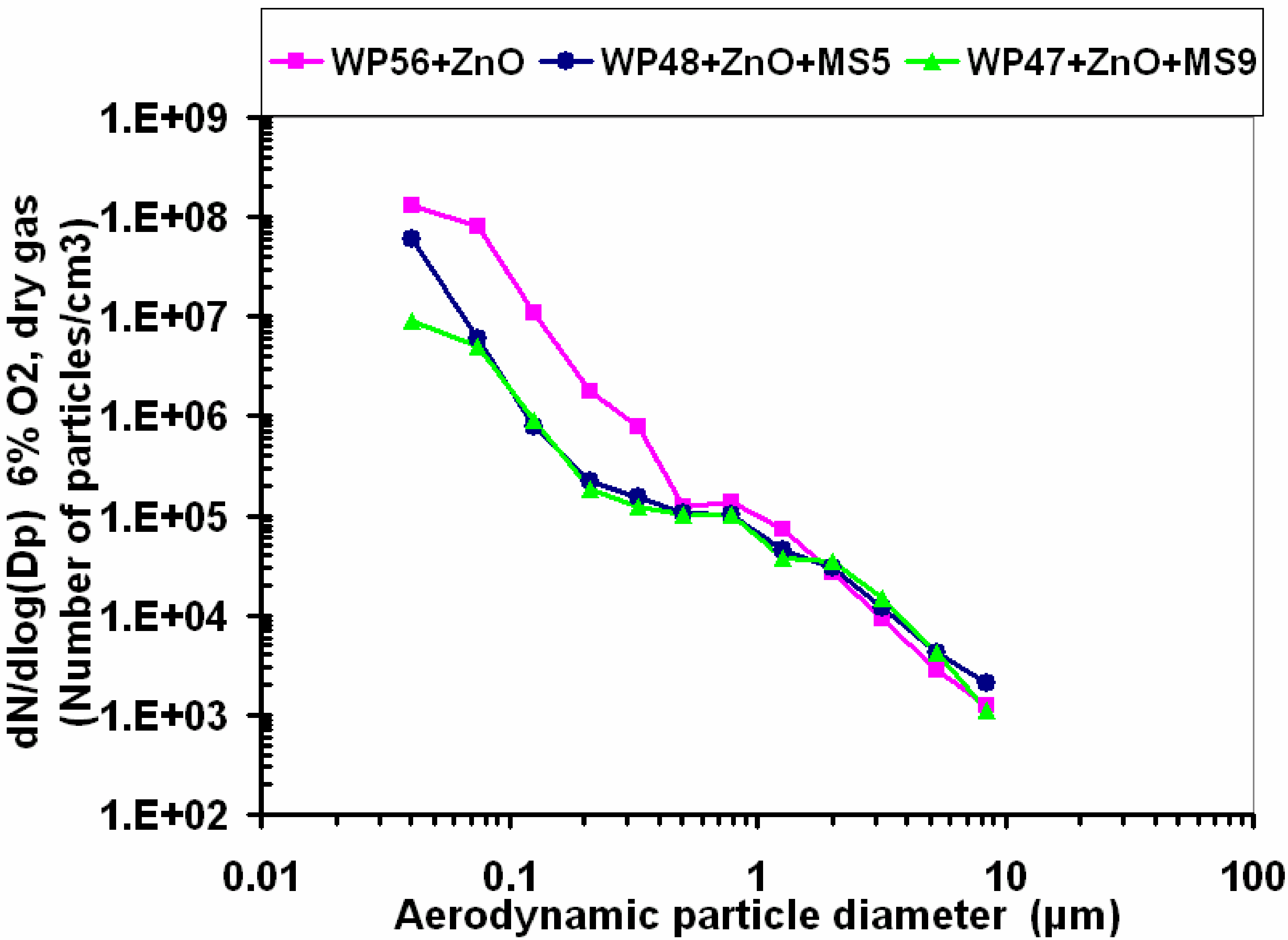
Results – Chemical analysis of the deposits



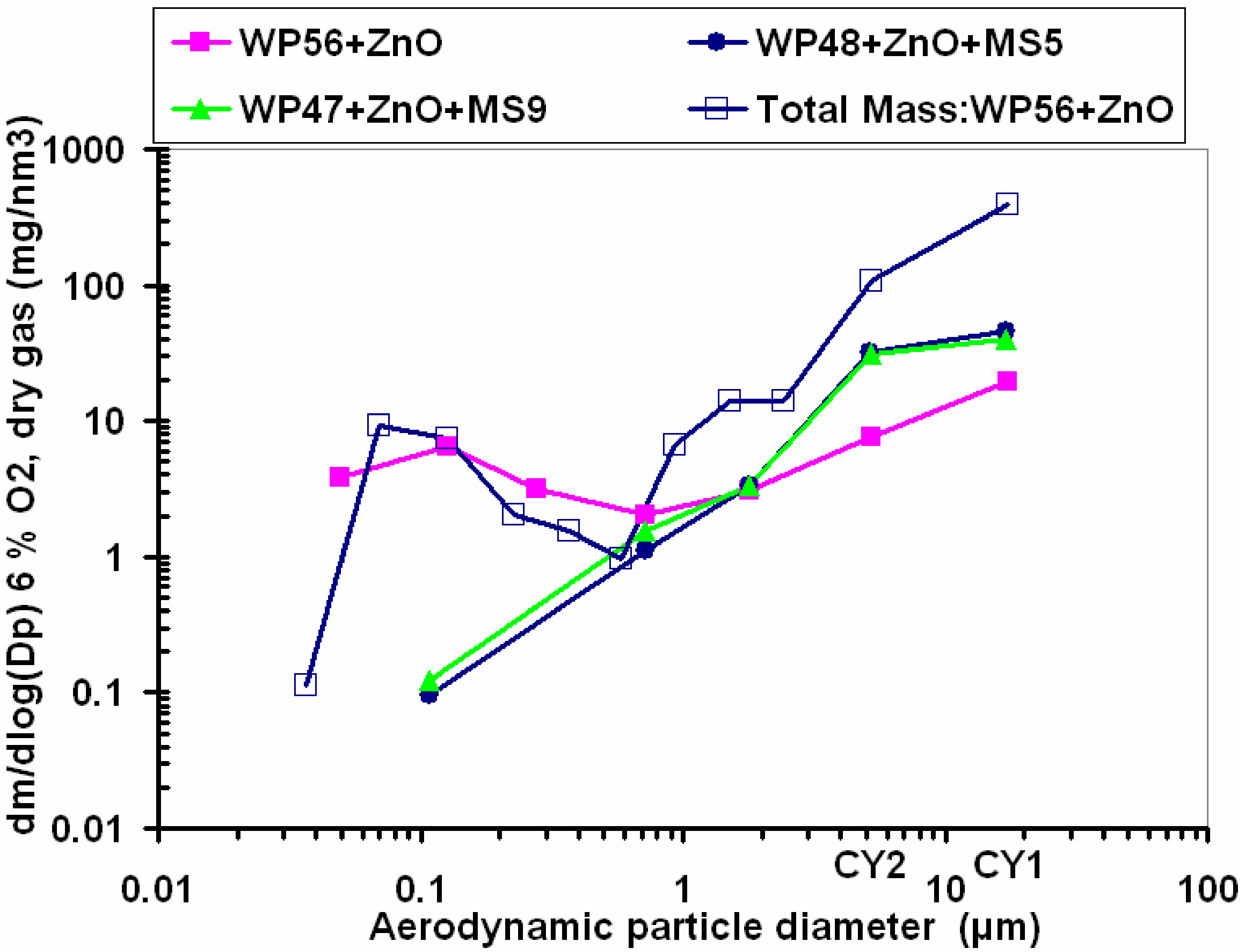
Results – Mass size distribution



Results – Number size distribution



Results - Sum of elements related to fouling (K, Na, Zn, Cl and S)



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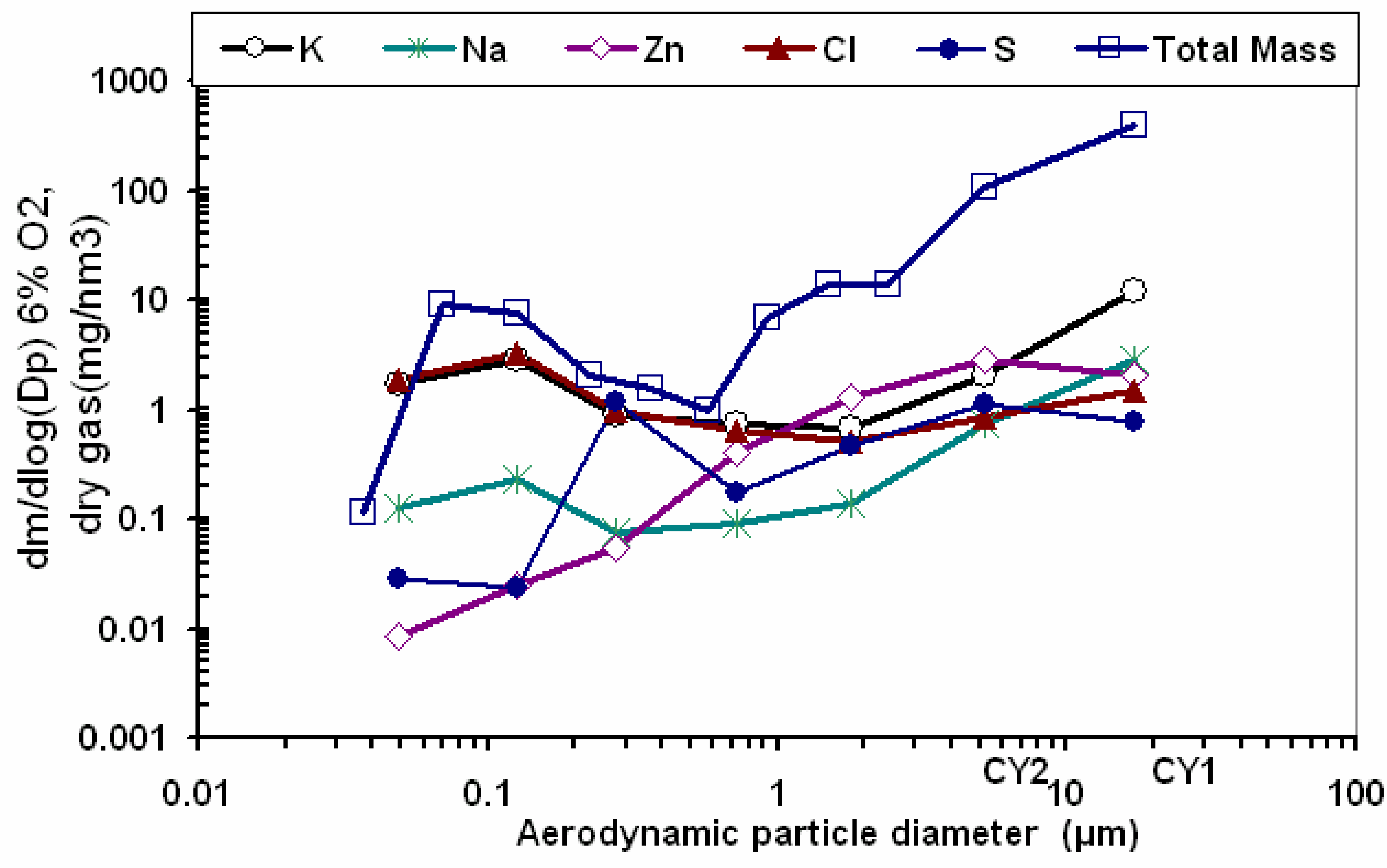
Results - Mass concentration of some critical elements in case: WP56+ZnO



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Discussion

Observations during sludge combustion:

- The deposit formation decreases radically
- The fouling related elements (mainly KCl and K2SO4) in the submicron particles are transported to the larger particles (Dp>1 µm)

Three explanations are going to be discussed for the reduction of the formation of solid deposits on tubes during addition of sludge

Discussion – Explanation 1: Sulphation

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$$2\ KCl + SO_2 + \tfrac{1}{2}O_2 + H_2O \Rightarrow K_2SO_4 + 2\ HCl$$

Test	S/Cl
WP38	1,35
WP33+MS13	6,4
WP56+ZnO	0,75
WP48+ZnO+MS5	3,75
WP47+ZnO+MS9	6,0
WP51+ZnO+HCl	0,15
WP44+ZnO+HCl+MS6	1
WP43+ZnO+HCl+MS10	2,52

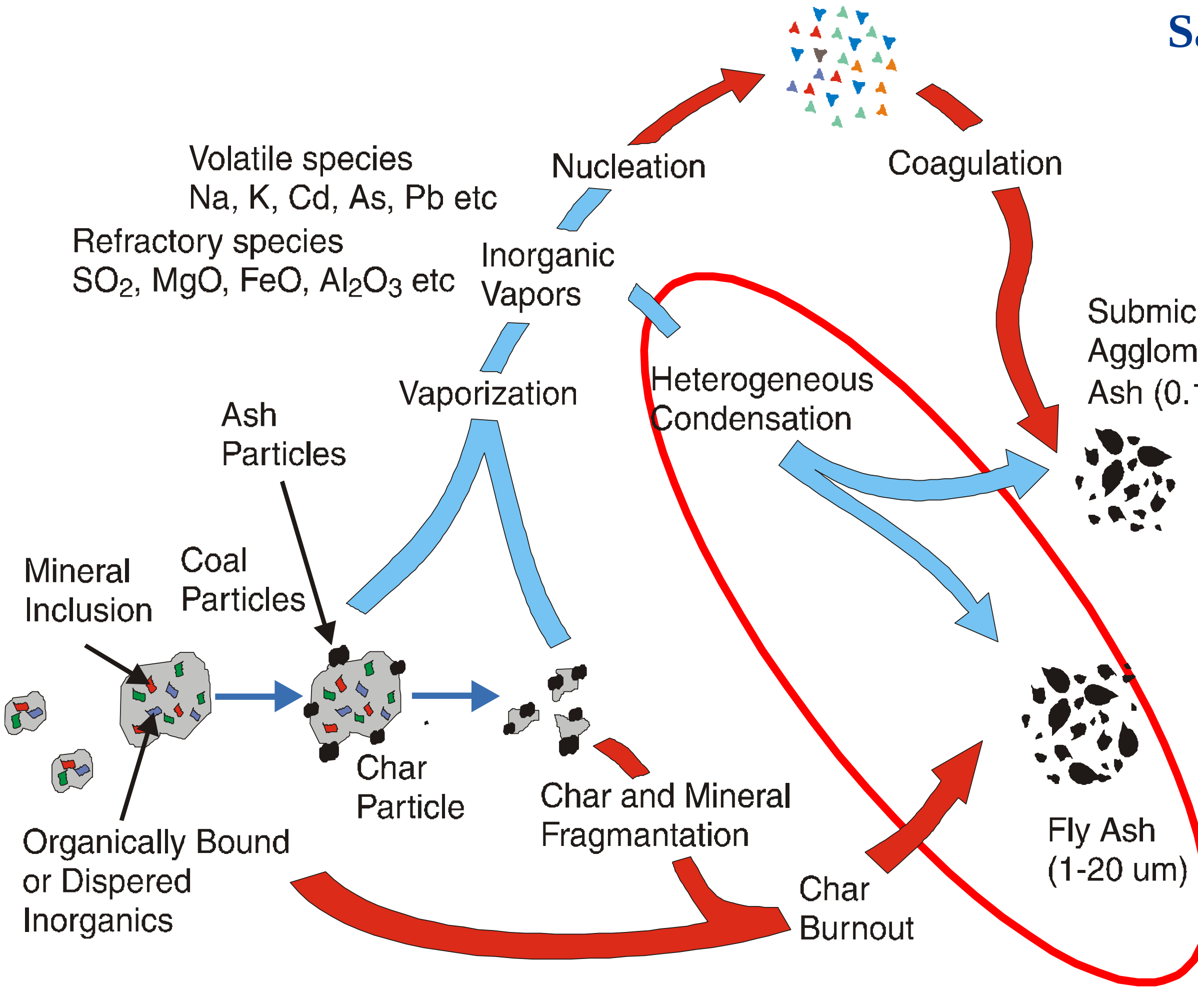
It has been stated[1] that when the fuel's molar ratio of S/Cl > 4, corrosion caused by chlorine will be avoided

Previous measurements have shown that these reactions cause a high mass concentration of submicron particles containing K_2SO_4

[1] Krause, 1986, Robinsson et al., 2002

Discussion –
Explanation 2: Heterogeneous condensation

Sarofim, A.F., Helble, J.J., 1993



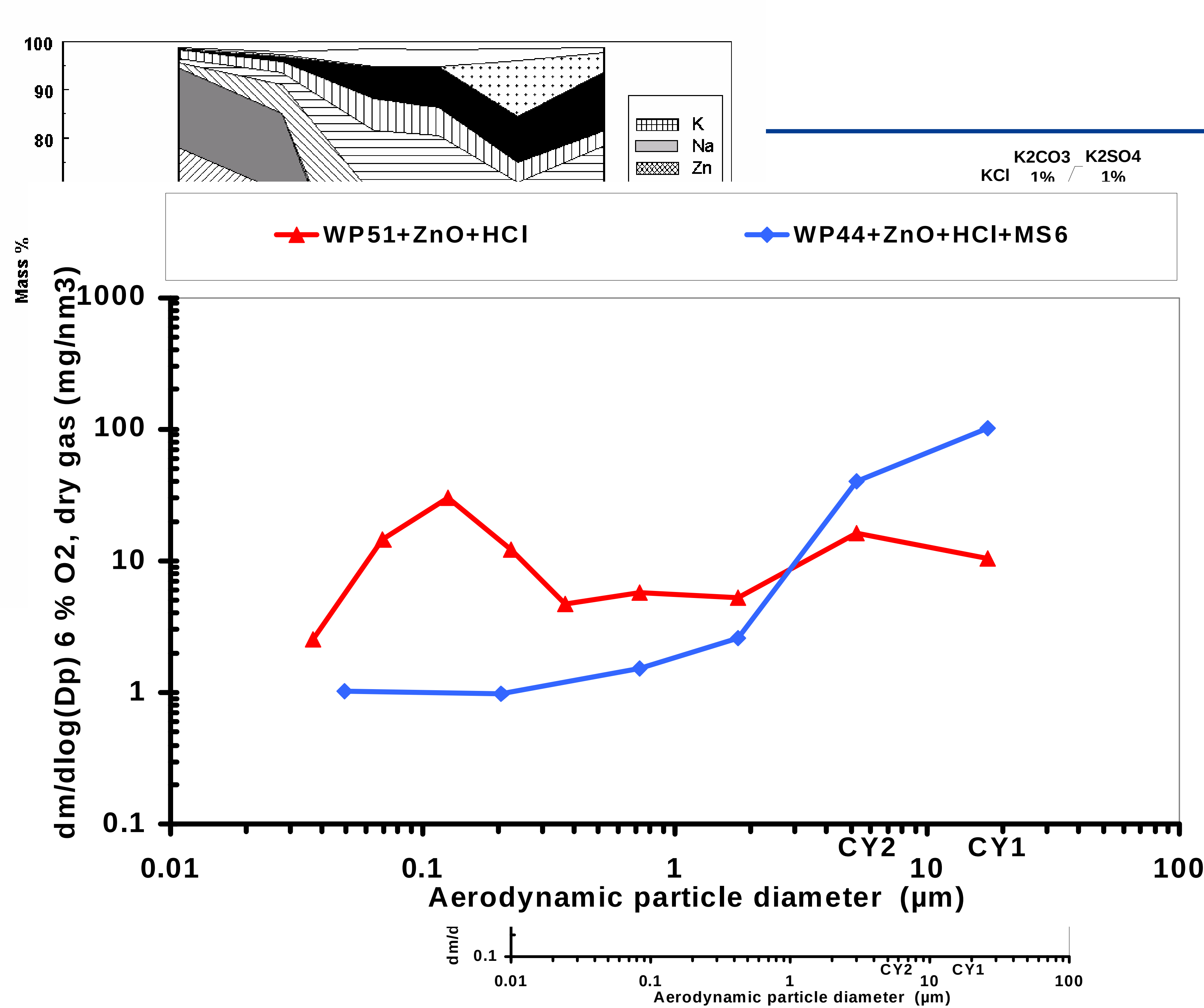
Suggested path when sludge is included in the combustion

Discussion – Explanation 3: Chemical reaction

- **The third possibility is a chemical reaction between the components of the sludge ash, particularly aluminium-silicon compounds, and potassium, liberating chlorine in the gaseous form (HCl).**

- **A suggestion in this direction has been advocated by Aho in connection to co-combustion of coal and biomass[1]**

[1] Aho and Silvennoinen, 2004, Aho and Ferrer, 2005



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Conclusions

- **The deposit formation decreases radically when sludge is added to the combustion**

- **The fouling related elements (mainly KCl) in the submicron particles are transported to the larger particles (Dp>1 µm)**

- **During high S/Cl ratios, the potassium is sulphated**

- **Some of the potassium is found on the larger particles as KCl and K2SO4 which indicates heterogeneous condensation**

- **Looking at the results from the elemental concentration of the larger particles during sludge combustion indicates that a major part of the potassium could have reacted with aluminum-silica compounds**

For more info: Åmand et al, Fuel 85 (2006) 1313-1322