Experiences with waste wood/sludge co-firing in Sweden

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Energimyndigheten

The story in short

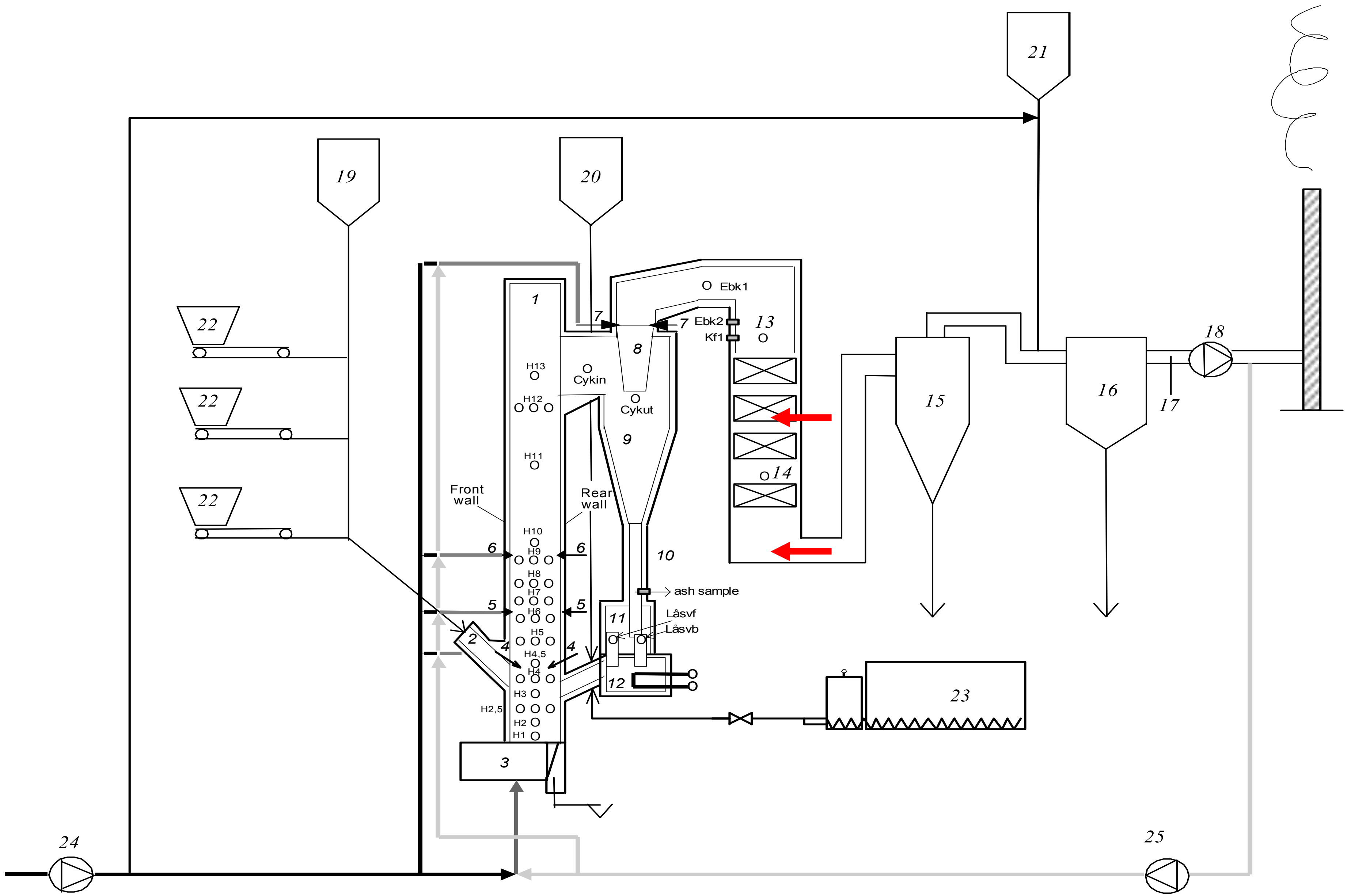
1) Waste wood is contaminated with Zn and Cl

   => increased problems with deposits

2) The deposit formation can be radically decreased by co-combustion with sewage sludge

3) What are the underlying mechanisms?

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

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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

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Experimental - Chemical analysis

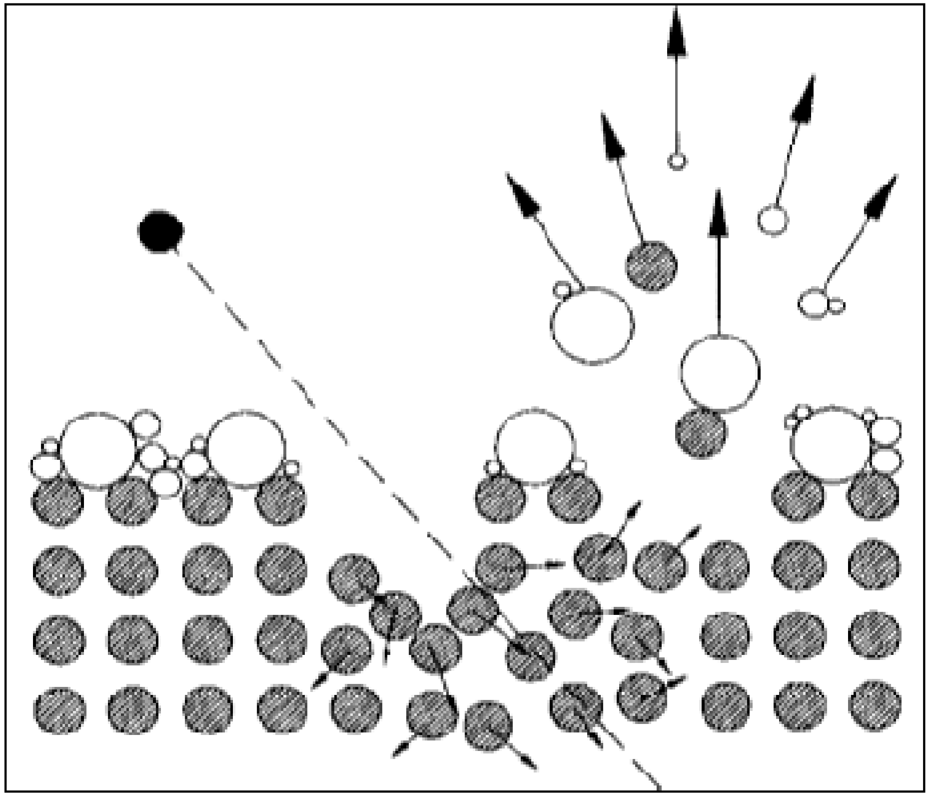
Some of the collected particle fractions have been characterized by using chemical analysis:

- 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

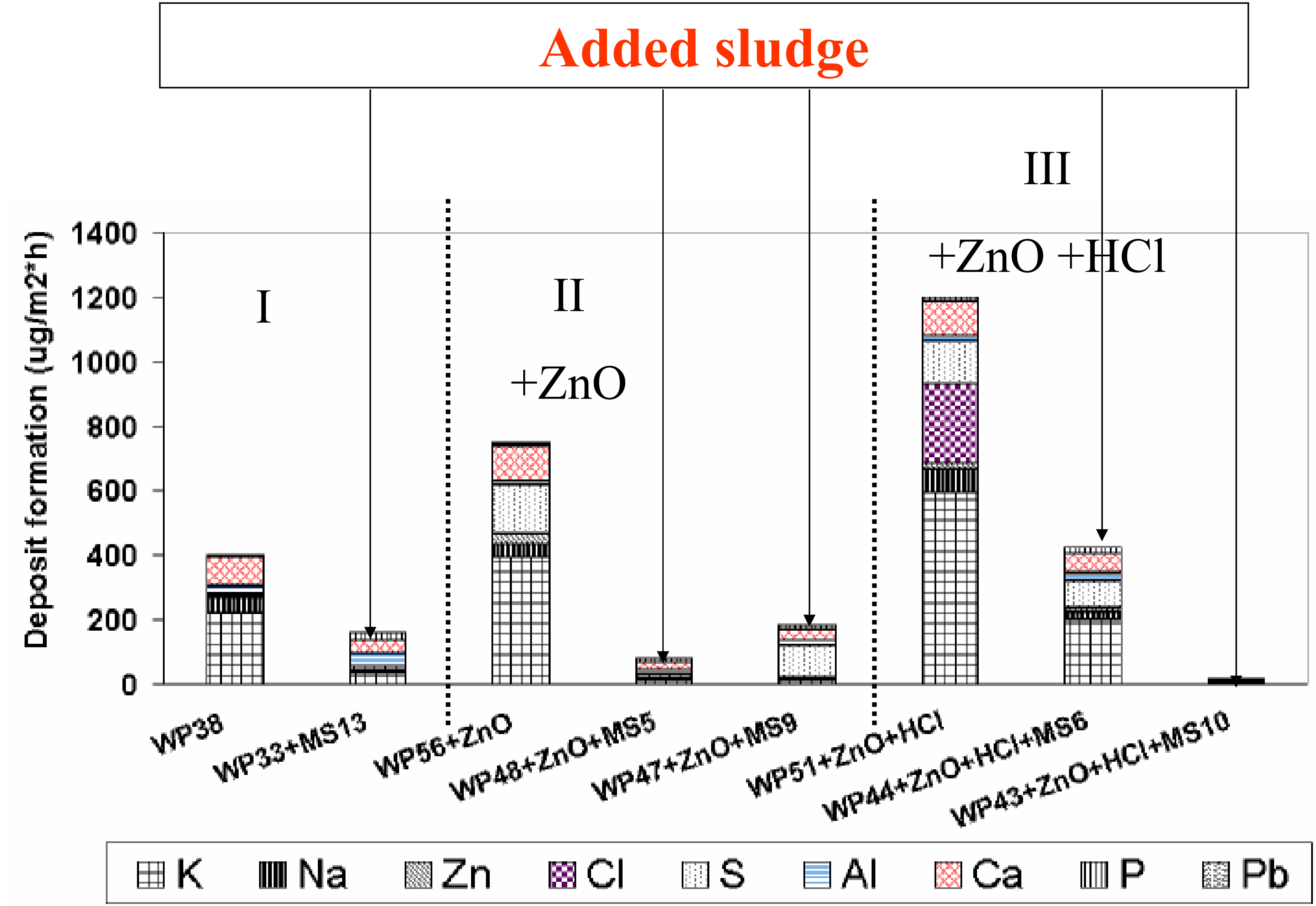
TOF-SIMS - Time-of-Flight Secondary Ion Mass Spectrometry



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



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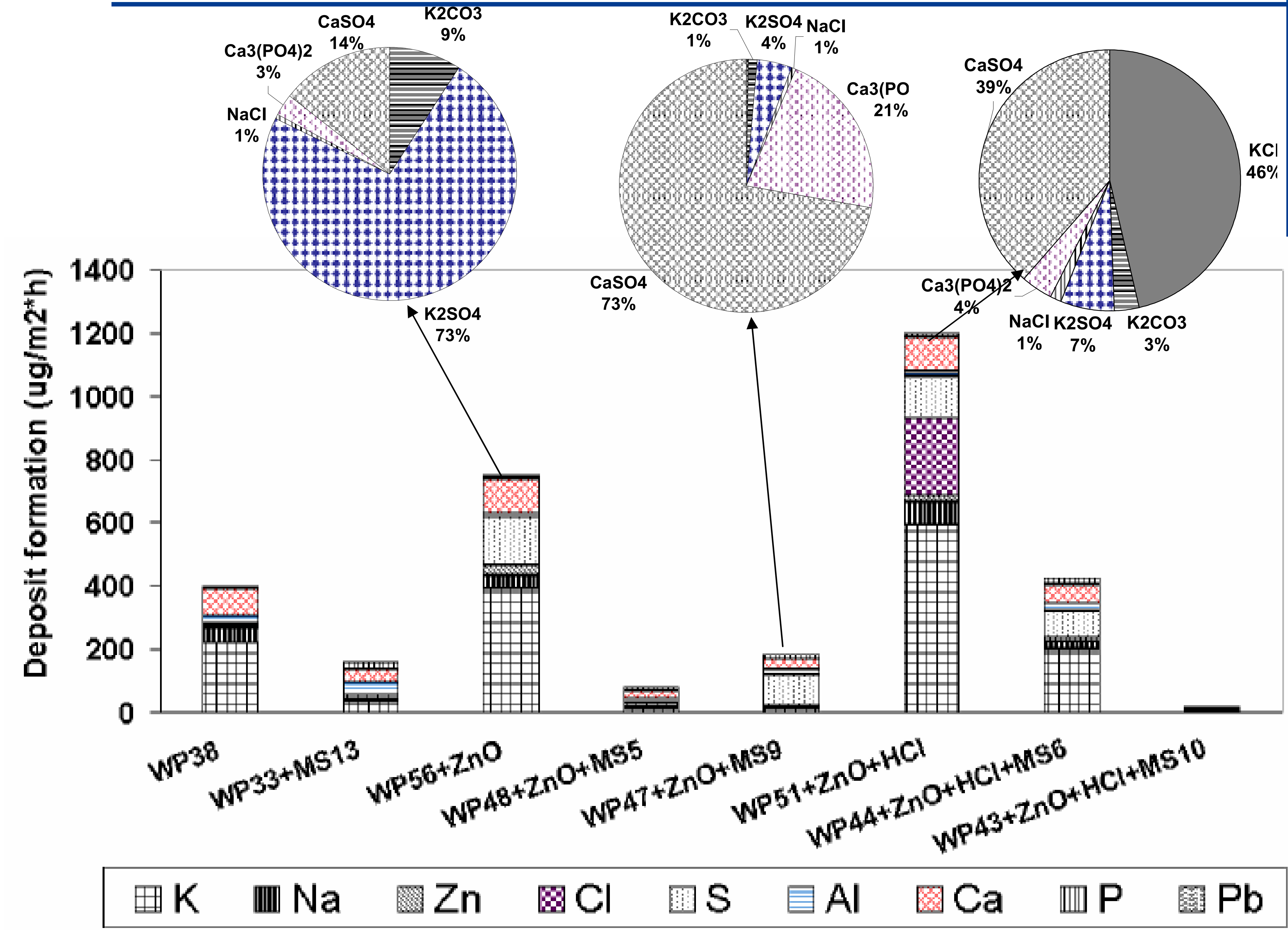
Results – Chemical analysis of the deposits



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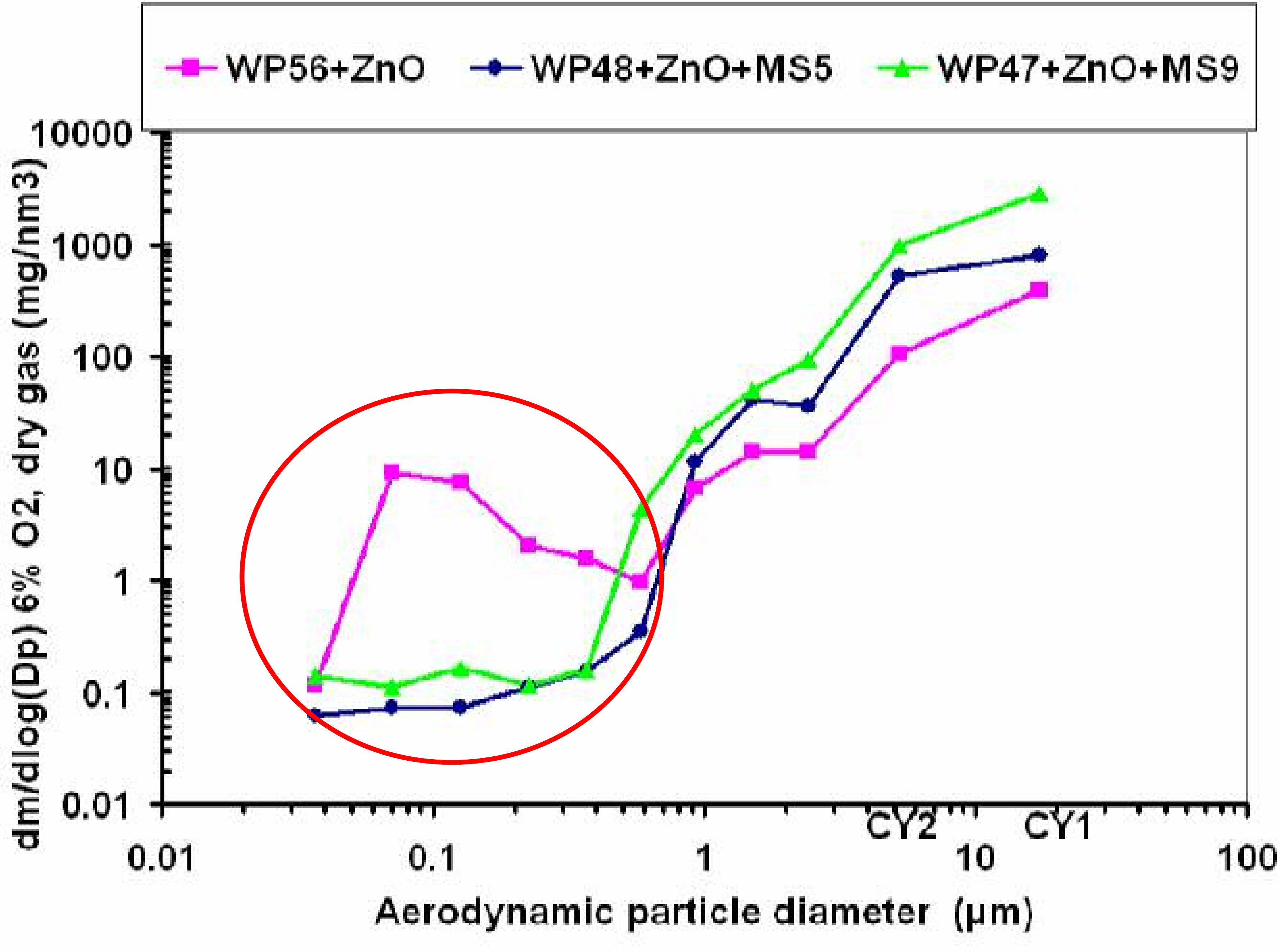
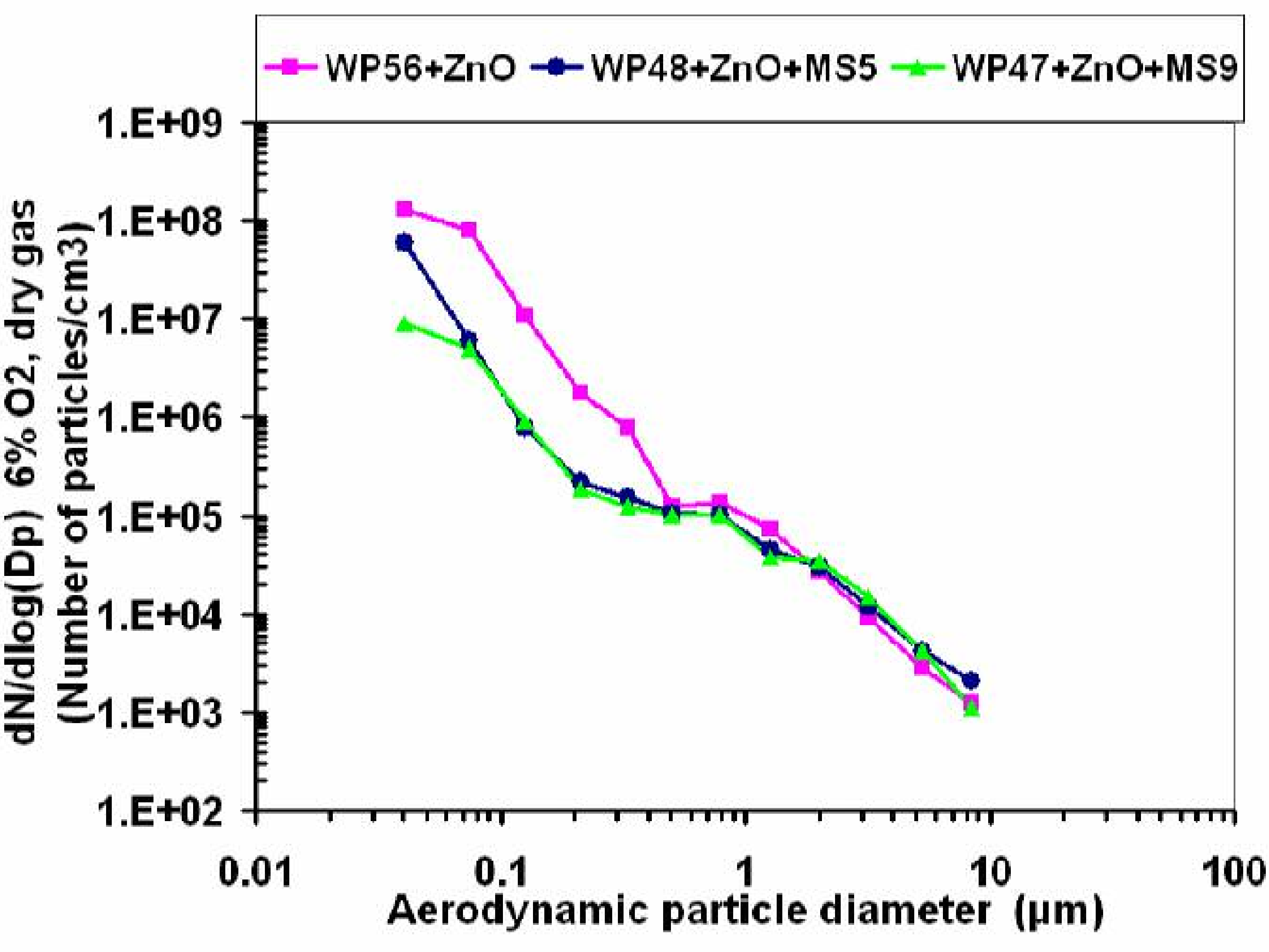
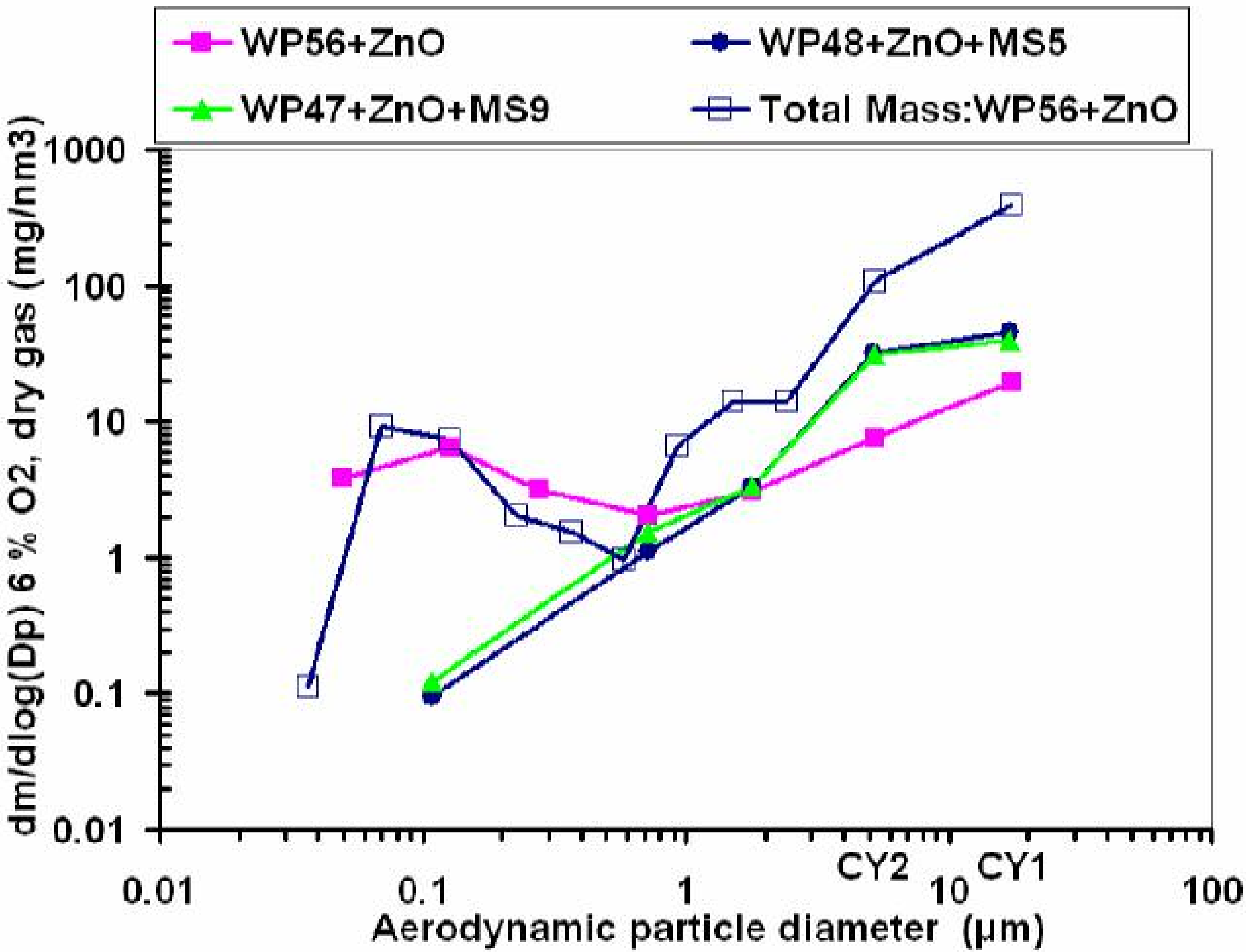
Results – Mass size distribution



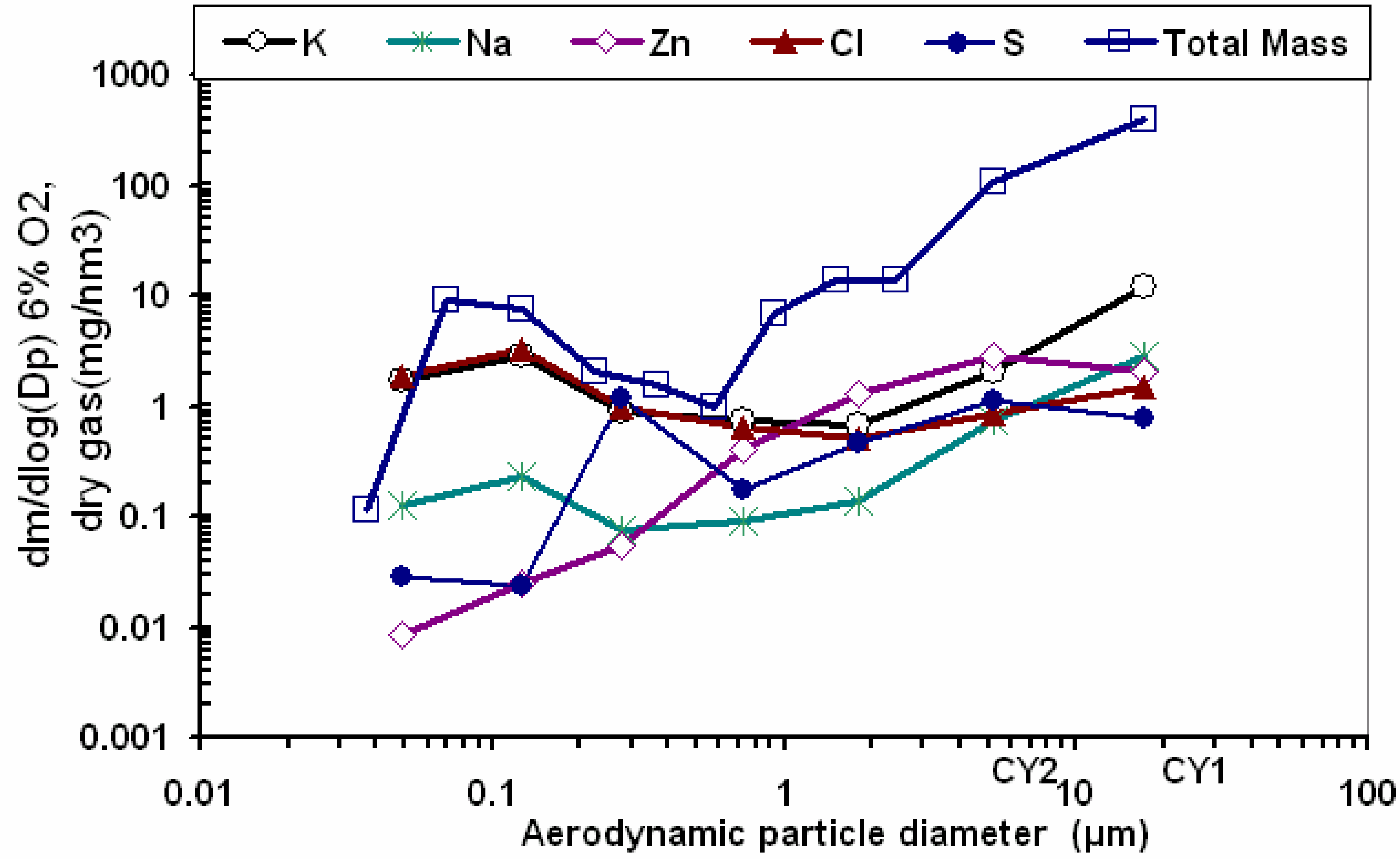
Results – Number size distribution



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



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

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

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

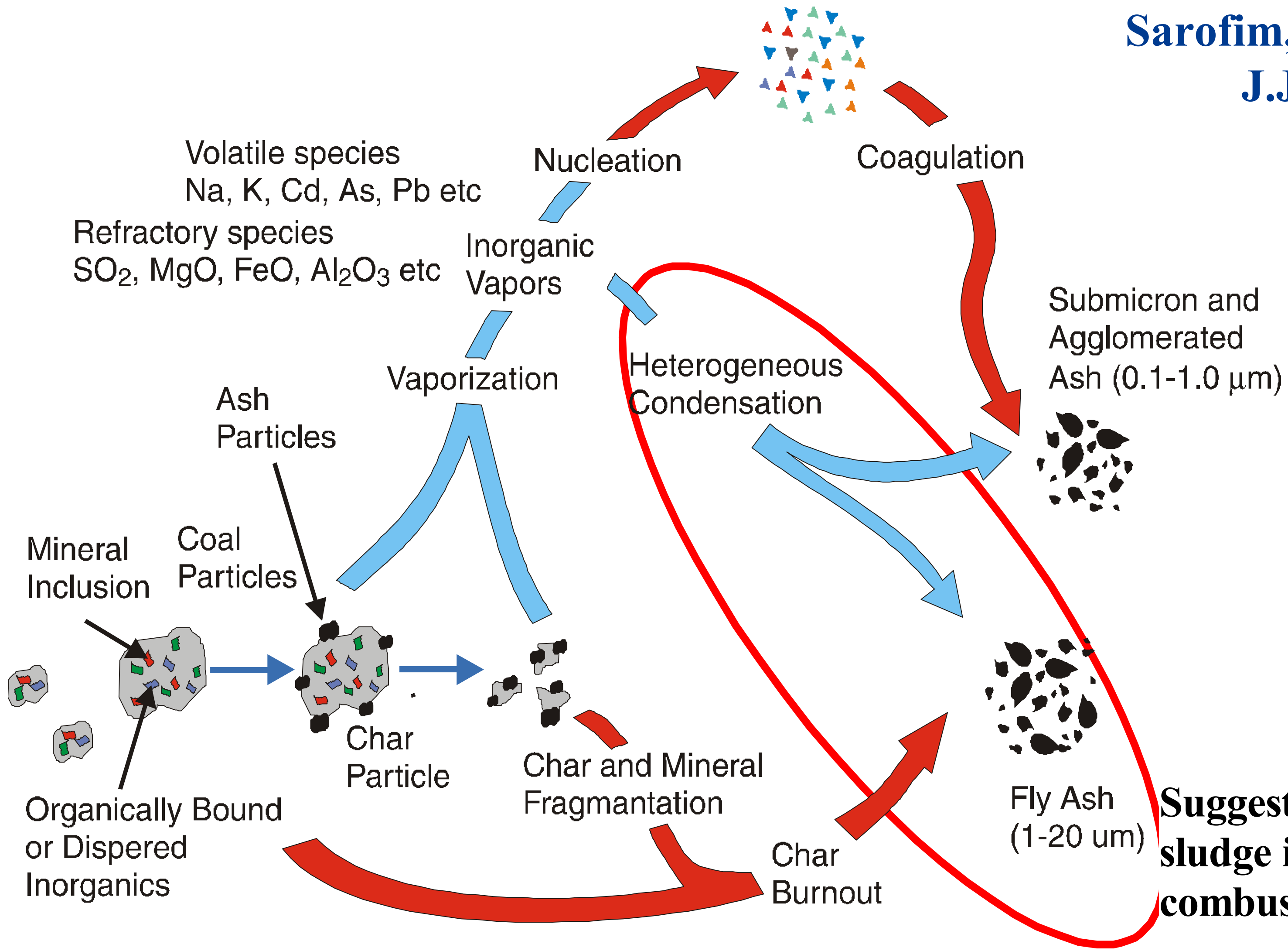
It has been stated[1] that when the fuel's molar ratio of S/Cl > 4, corrosion caused by chlorine will be avoided

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



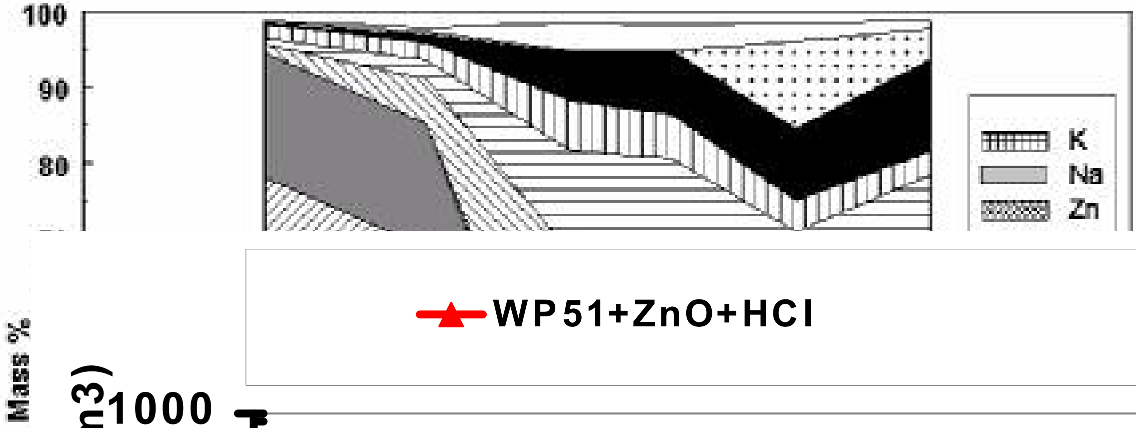
Suggested path when sludge is included in the combustion

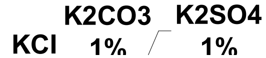
Discussion – Explanation 3: Chemical reaction

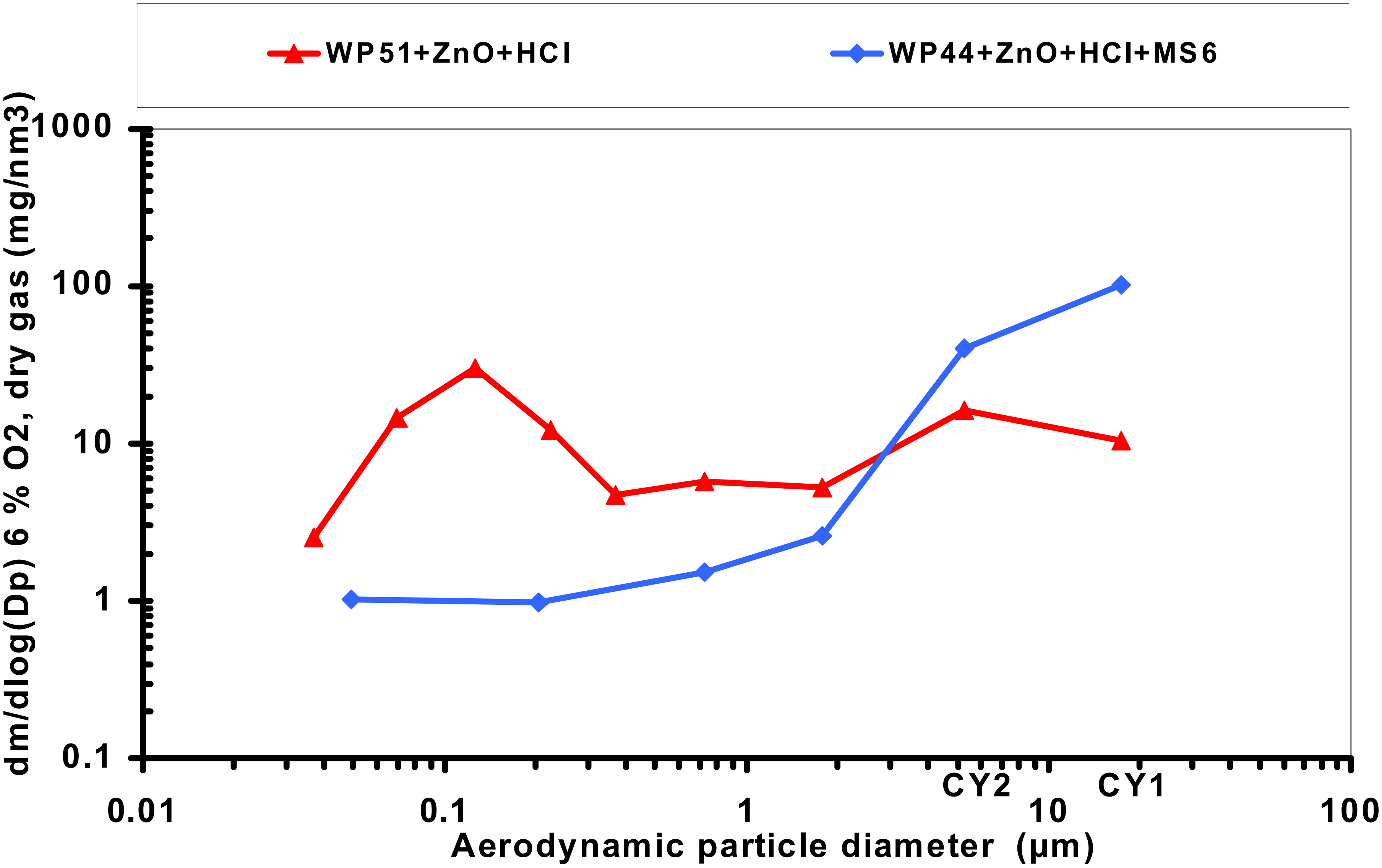
- The third possibility is a chemical reaction between the components of the sludge ash, particularly aluminium-silicon compounds, and potassium, liberating chlorine in the gaseous form (HCl).

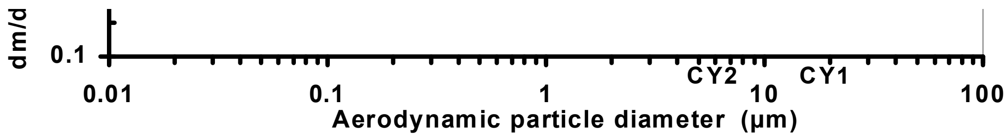
- A suggestion in this direction has been advocated by Aho in connection to co-combustion of coal and biomass[1]

[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

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