Formation & Reduction of Pollutants in FBC:

From Heavy Metals, Particulates, Alkali, NO_x, N_2O, SO_x, HCl

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Contents

- Co-combustion
- Nitrogen Oxides NO, NO_2, N_2O
- Sulfur Oxides SO_2, SO_3
- HCl, Alkali, Heavy Metals, Dioxins
- Particulates
- Conclusions

Co-combustion

1. General definition:

Firing together
any fuels in the same plant.

2. Limited definition:

Firing together
low grade fuel with coal in the same plant.

3. Further limited definition – of greatest significance:

Firing together
biofuel, waste with coal in in the same combustor.

Nitrogen Oxides NO, NO_2, N_2O

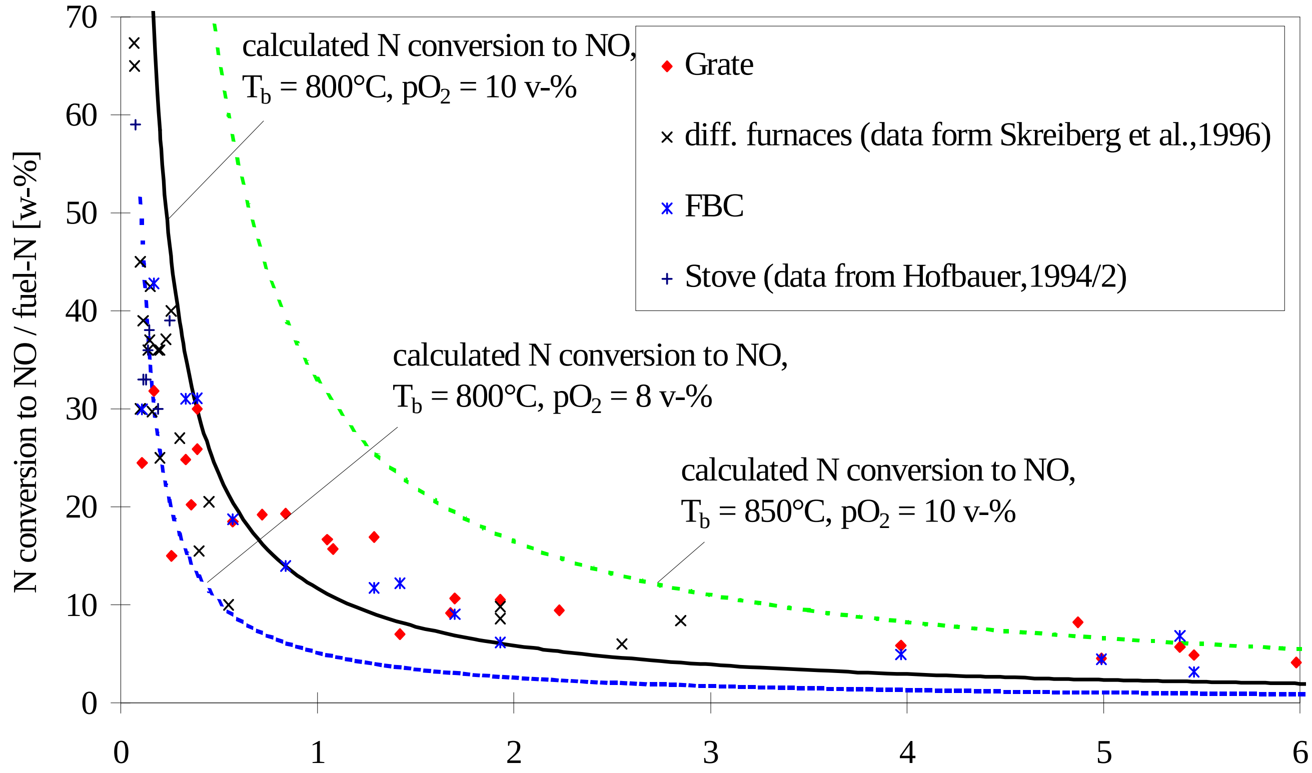
Typical Nitrogen contents of fuels

Analysis (daf)	ANT	LVB	MVB	HVB	SUB	LIG	PT	WD	WPB	SEW	PE
carbon [w-%]	93	87	88	83	67	66	60	50	48	56	85
nitrogen [w-%]	1.2	1.8	1.6	1.5	1.3	1.2	1.5	0.18	2.77	6.3	0.07

ANT - anthracite, LVB - low volatile bituminous coal, MVB - medium volatile bituminous coal, HVB - high volatile bituminous coal, SUB - sub-bituminous coal, LIG - lignite, PT - peat, WD - wood, WPB - wooden pressboard, SEW - sewage sludge, PE - polyethylene.

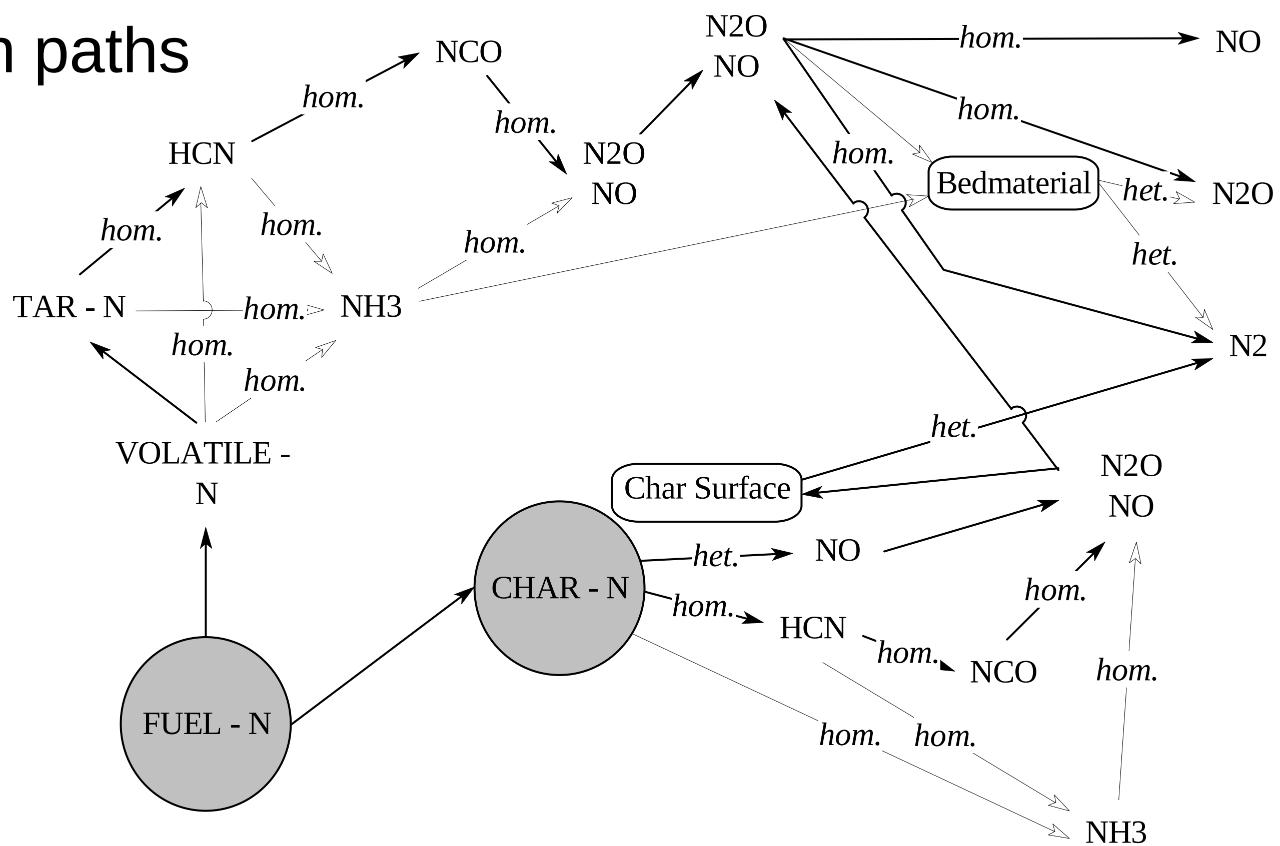
Nitrogen Oxides NO, NO_2, N_2O

Conversion of fuel-N to NO



Nitrogen Oxides NO, NO_2, N_2O

Main reaction paths



Nitrogen Oxides NO, NO_2, N_2O

Indirect interactions with halogen chemistry via pool of radicals

CO Oxidation:

$$CO + OH = CO_2 + H$$

Inhibition of radicals:

$$I + I + M = I_2 + M$$

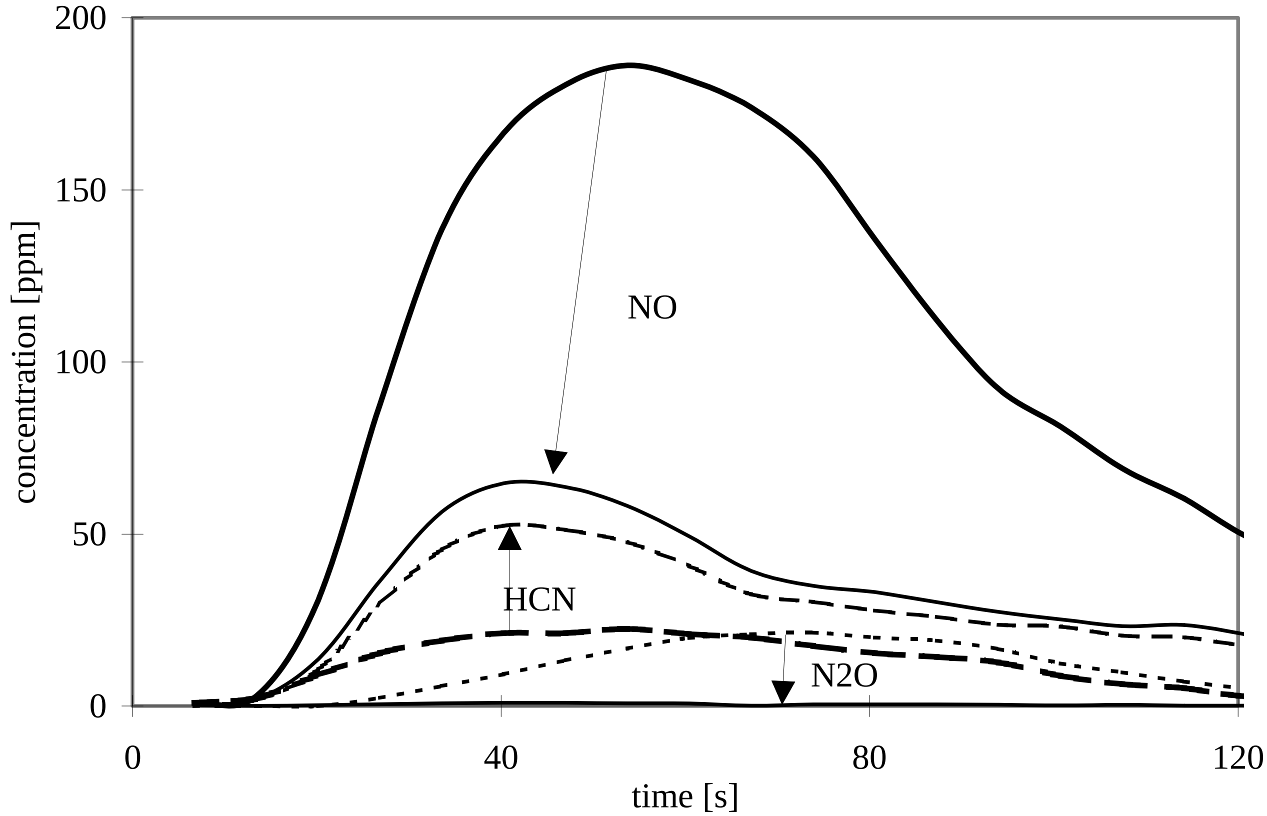
$$I_2 + H = HI + I$$

$$\underline{HI + OH = H_2O + I}$$

total: $\mathbf{H + OH = H_2O}$

Nitrogen Oxides NO, NO_2, N_2O

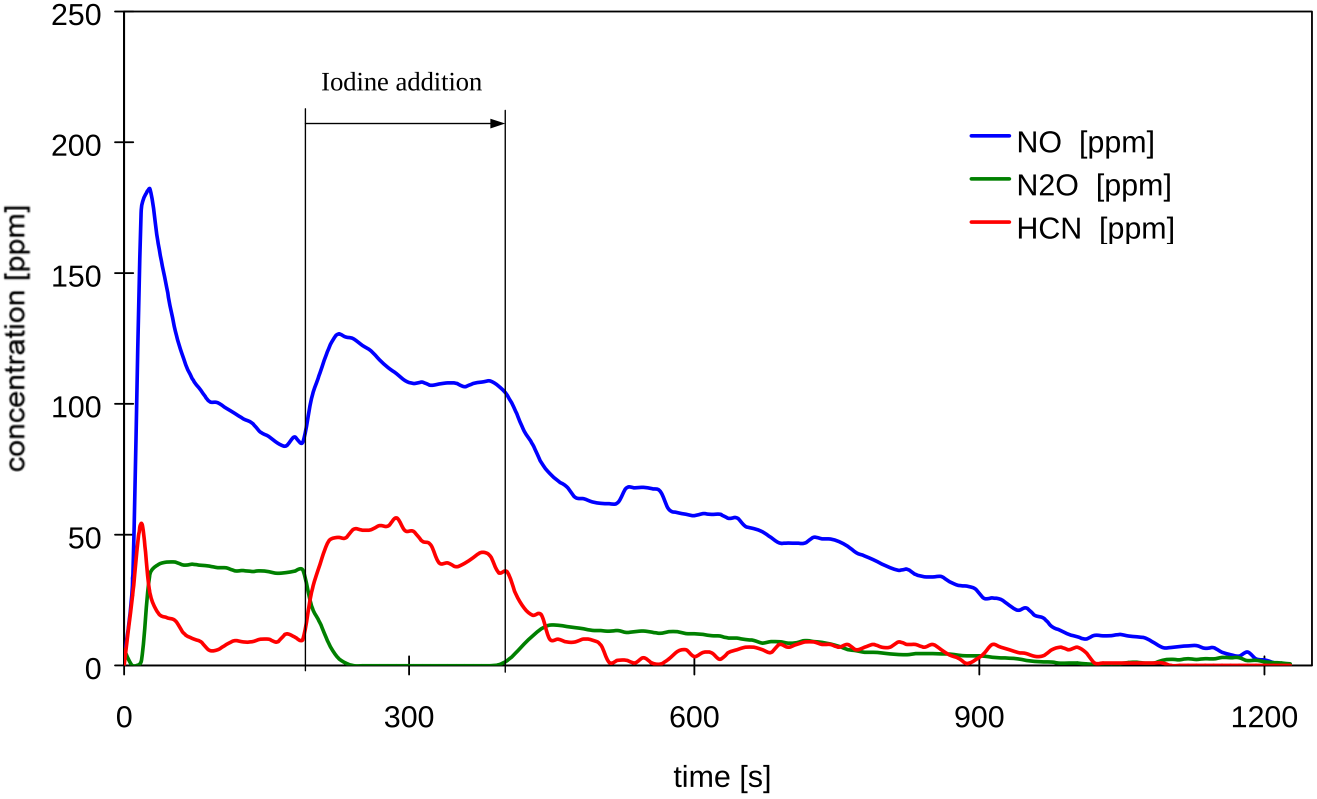
Iodine addition to single fuel particle during devolatilization



Winter et al. 1999

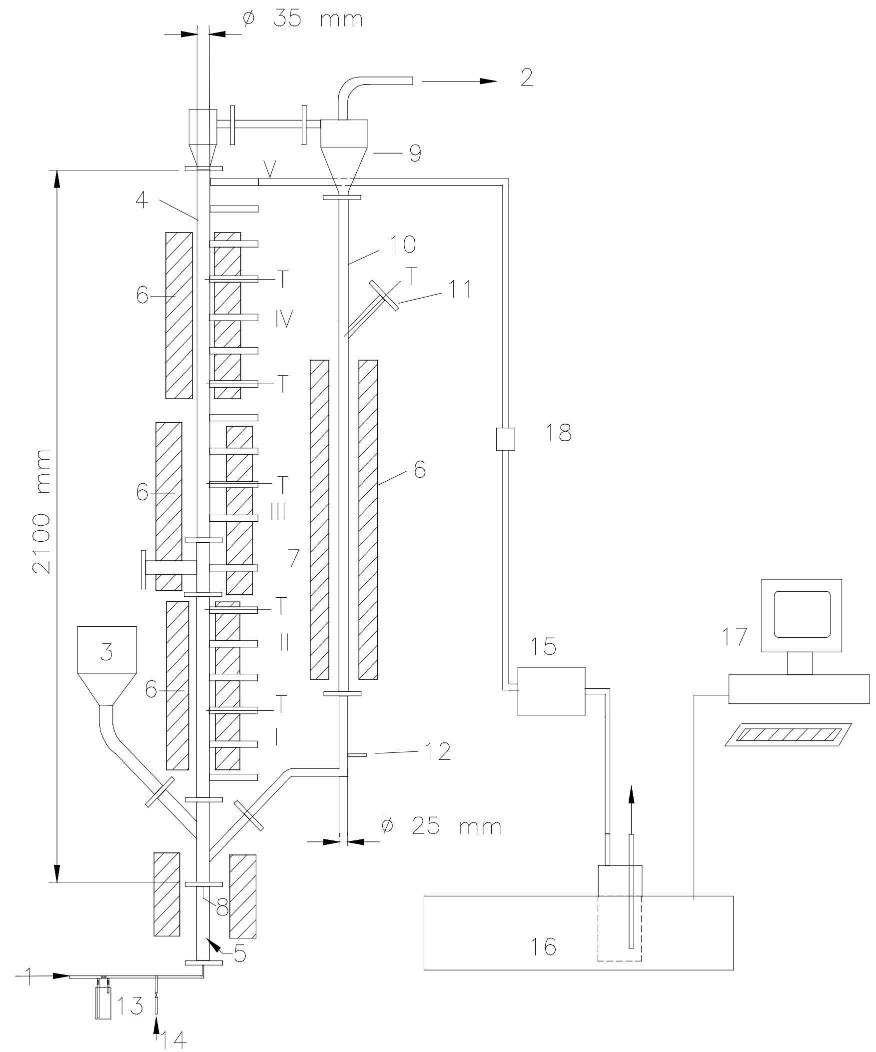
Nitrogen Oxides NO, NO_2, N_2O

Iodine addition to single fuel particle during char combustion



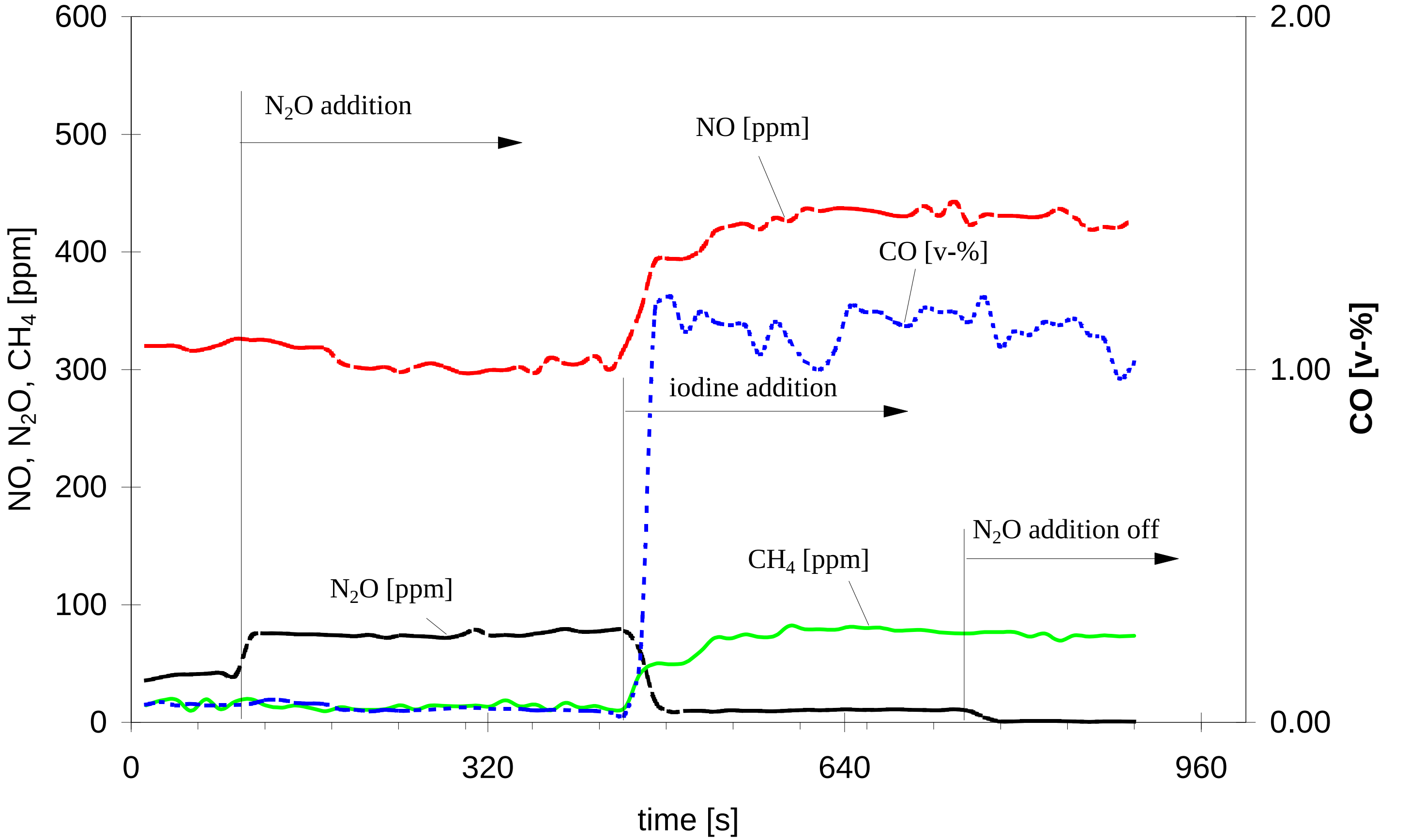
Nitrogen Oxides NO, NO_2, N_2O

Laboratory-scale CFBC at TU-Vienna:



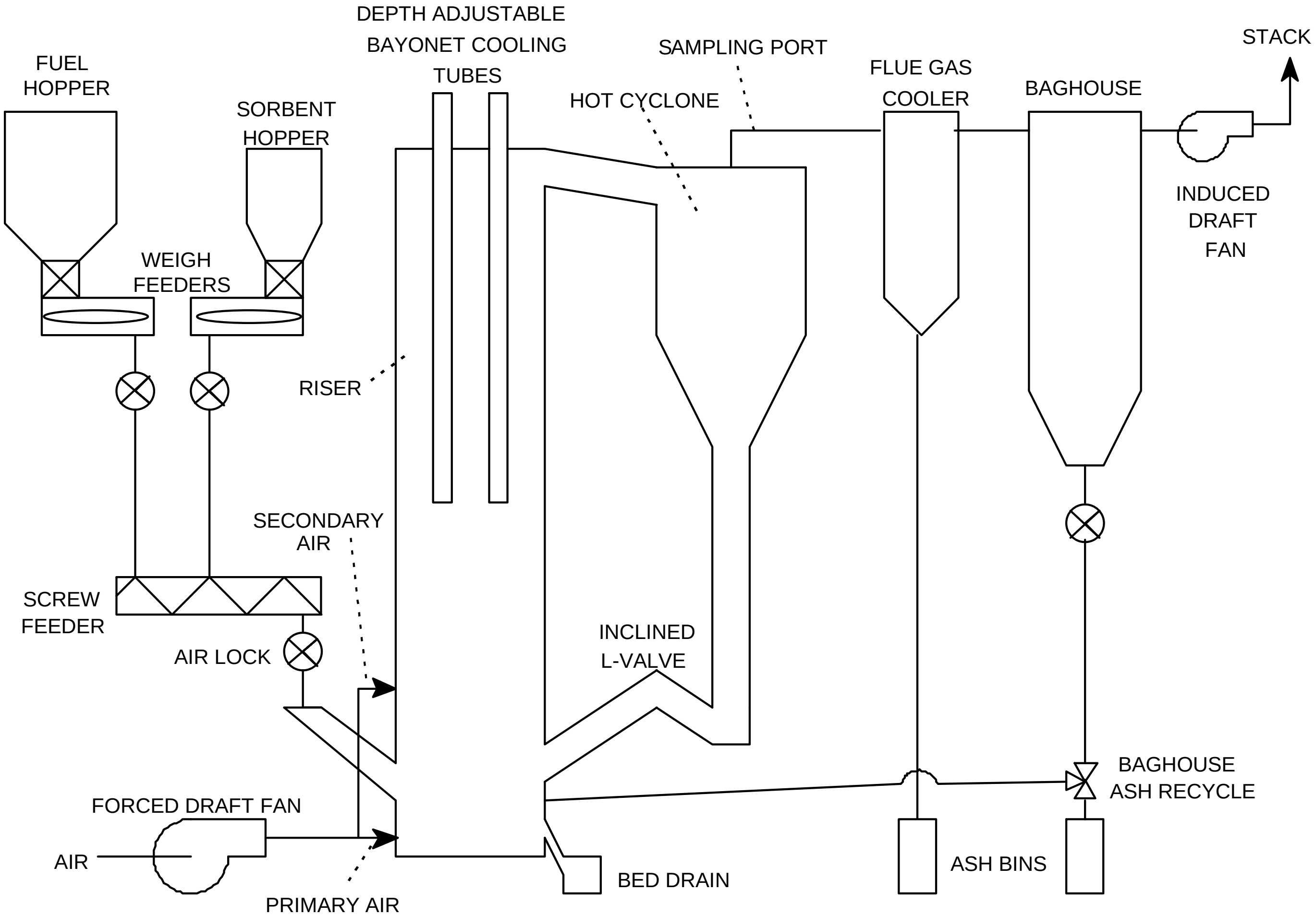
Nitrogen Oxides NO, NO_2, N_2O

Iodine addition into lab-scale CFBC burning coal



Nitrogen Oxides NO, NO_2, N_2O

pilot-scale CFBC at CANMET:



Nitrogen Oxides NO, NO_2, N_2O

Pollutants´ concentrations in pilot-scale CFBC burning coal with and without iodine addition

	before cyclone				after cyclone			
Run	**CO** (%)	**NO** (ppm)	**N_2O** (ppm)	**HC** (ppm)	**CO** (%)	**NO** (ppm)	**N_2O** (ppm)	**HC** (ppm)
15	0.40	93	na	2730	0.05	72	134.5	0
15I	1.93 ↑	442 ↑	16.5	8310	1.59 ↑	295 ↑	26.5 ↓	7400

Nitrogen Oxides NO, NO_2, N_2O

Main parameters

increasing parameters	**NO emission**	**N2O emission**
Temperature	↑	↓
Volatile matter content	↓ (BFBC) ↑ (CFBC)	↓
Nitrogen content	↑	↑
Excess air	↑	↑
Air staging	↓	↓
Limestone addition	↑	↓
SO2 concentration	↓	↑
SNCR	↓	↑

Sulfur Oxides SO_2, SO_3

Typical Sulfur contents of fuels

Analysis (daf)	anthracite	coals	lignite	peat	straw	wood	sewage sludge	tire waste	petroleum coke
sulfur [w-%]	1	1	0.5-3	0.5	0.1	0.02	0.8	1.5	5-7

Sulfur Oxides SO_2, SO_3

Main reactions

$CaCO_3 \Rightarrow CaO + CO_2$	R1	calcination
$CaO + SO_2 \Rightarrow CaSO_3$	R2	sulfation
$CaSO_3 + \frac{1}{2} O_2 \Rightarrow CaSO_4$	R3	oxidation

Sulfur Oxides SO_2, SO_3

Effects on the pool of radicals:

$$SO_2 + H + M \leftrightarrow HSO_2 + M$$
$$HSO_2 + H \leftrightarrow H_2 + SO_2$$
$$HSO_2 + OH \leftrightarrow H_2O + SO_2$$

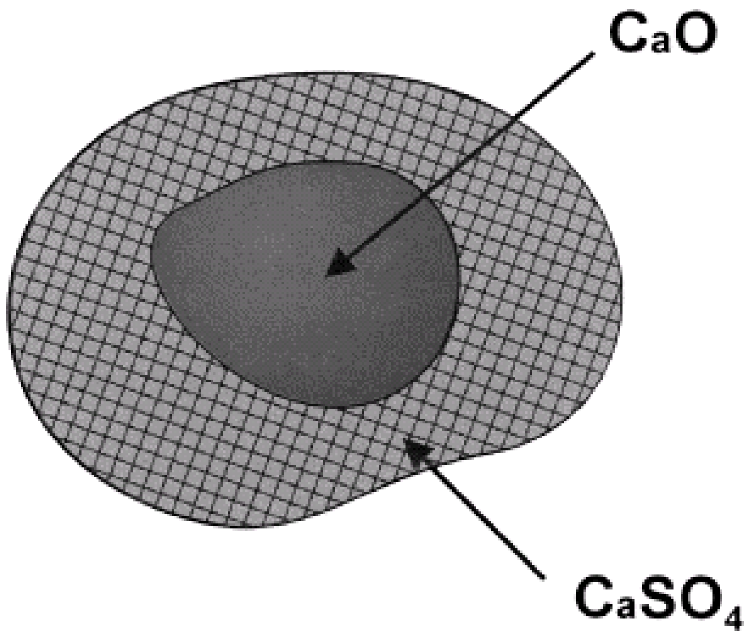
$$SO_2 + O \leftrightarrow SO_3$$
$$SO_3 + O \leftrightarrow SO_2 + O_2$$

Miccio et al. 2001

Sulfur Oxides SO_2, SO_3

Phenomenology

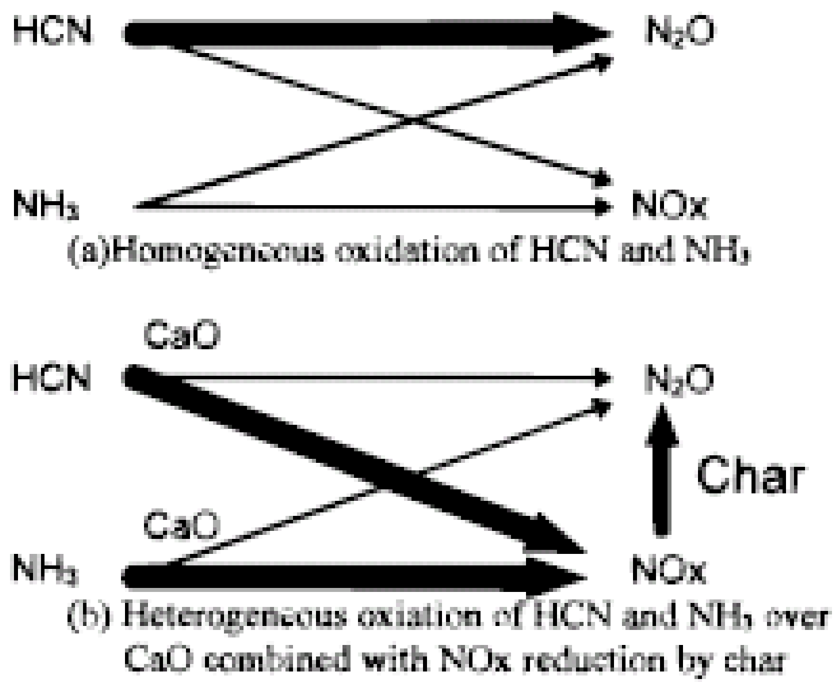
Formation of
dense $CaSO_4$ shells
limit conversion



Anthony and Granatstein 2001

Sulfur Oxides SO_2, SO_3

Heterogeneous catalytic effects with CaO:



Shimizu et al. 2000

HCl, Alkali, Heavy Metals, Dioxins

Typical Chlorine contents of fuels

Ulitmate Analysis (dry fuel)	hard coals	brown coals	peat	wheat straw	wood	sewage sludge ash	waste wood	Meat Bone Meal
chlorine [w-%]	0.01 – 0.2	0.005 – 0.1	0.01	0.5	<0.01	0.01	0.3	0.35

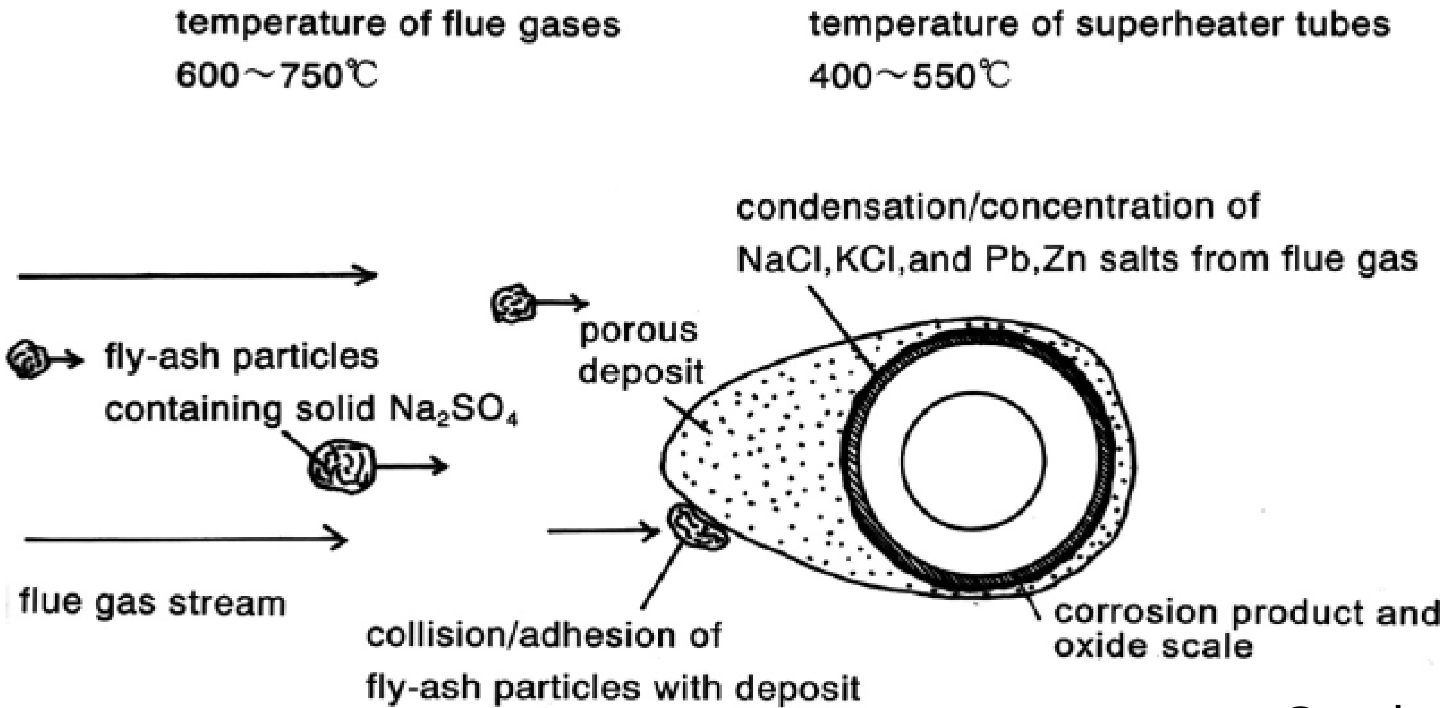
HCl, Alkali, Heavy Metals, Dioxins

Important reactions, direct interactions

$4HCl + O_2 \Rightarrow 2Cl_2 + 2H_2O$	R4	conversion to Cl_2 (Deacon reaction)
$MeCl + H_2O \Rightarrow HCl + MeOH$	R5	Me = Na, K interaction with alkali chemistry
$2MeCl + SO_2 + H_2O + ½ O_2 \Rightarrow Me_2SO_4 + 2HCl$	R6	interaction with $CaCl_2$ and sulfur chemistry
$2MeCl + H_2O + ½ O_2 \Rightarrow Me_2CO_3 + 2HCl$	R7	interaction with alkali-chlorides
$CaCl_2 + SO_2 + H_2O + ½ O_2 \Rightarrow CaSO_4 + 2HCl$	R8	interaction with $CaCl_2$ and sulfur chemistry
$SO_2 + Cl_2 + H_2O \Rightarrow SO_3 + 2HCl$	R9	interaction with sulfur chemistry, formation of SO_3
$Al_2O_3.2SiO_2 + 2MeCl + H_2O \Rightarrow Me_2O.Al_2O_3.2SiO_2 + HCl$	R10	interaction with alumina silicates

HCl, Alkali, Heavy Metals, Dioxins

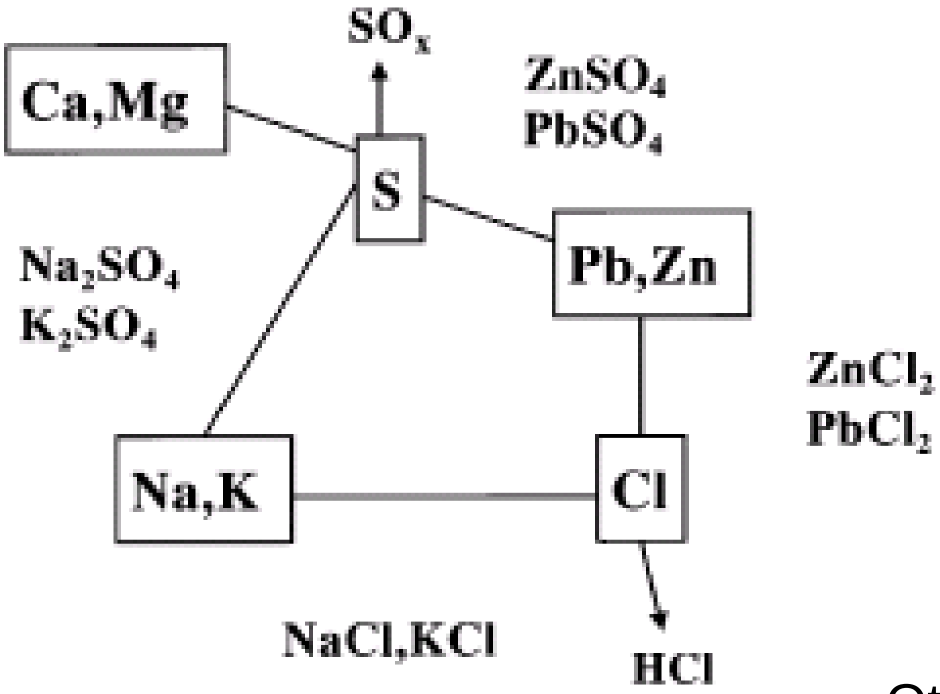
Corrosive salt formation, physical interactions



Otsuka 2008

HCl, Alkali, Heavy Metals, Dioxins

Interaction of chemistry



Otsuka 2008

Particulates

- Particulate Matter (PM) ... ultrafine solid particles, droplets
- PM10, PM2.5 ... harmful to respiratory system
- not much knowledge
- some on-going studies

Conclusions

- In fluidized bed combustors a wide range of fuels is utilized and burned at the same time

- The fuel is the main source for the pollutants formation of NO_x, N_2O, SO_x, HCl, heavy metals and alkali

- Pollutants may lead to difficulties in operation e.g. slagging, fouling and catalyst deactivation and health problems and pollution of the environment

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Conclusions

- It has been shown that a strong interaction between the different pollutants’ chemistry exists

- Homogeneous reactions in the gas phase (direct and indirect interactions), heterogeneous and catalytic surface reactions (on solid and liquid surfaces) as well as physical processes may be of importance

- There is a significant lack of knowledge considering pollutants’ chemistry interactions.

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Thank you for your attention!

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