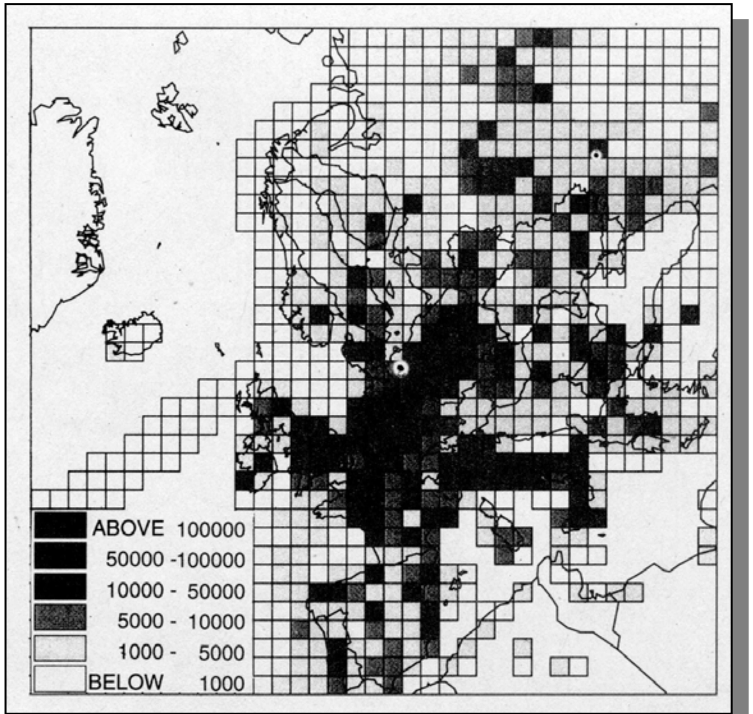
NITROGEN #1

- NOx and NH_3 emissions, NOx deposition
- Nitrogen in fuels
- Formation and reduction of NOx during burner combustion
- Low NOx technology : low NOx burners, fuel/air staging, ...
- Flue gas treatment for NOx reduction: SCR, SNCR, other

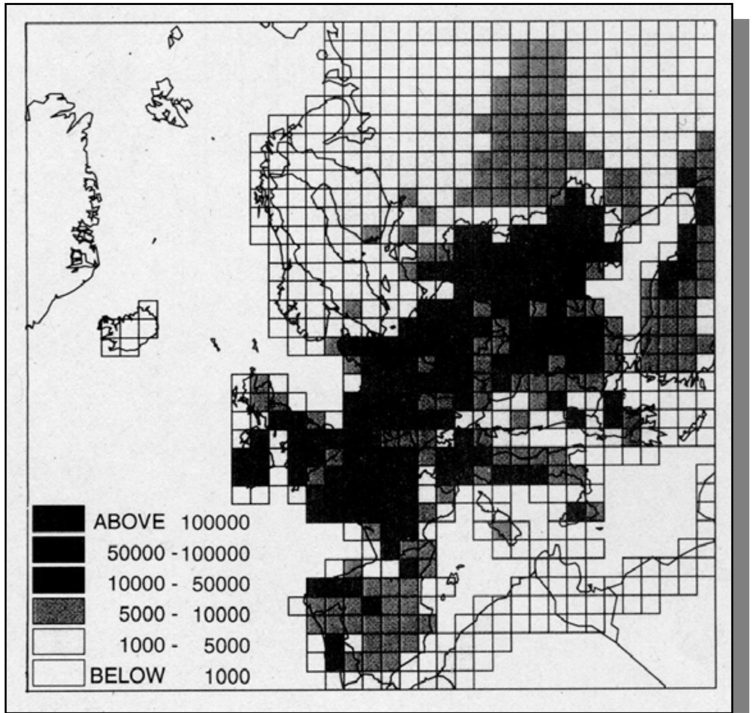
NOTE : $NOx = NO + NO_2$

see: www.hut.fi/~rzevenho/gasbook

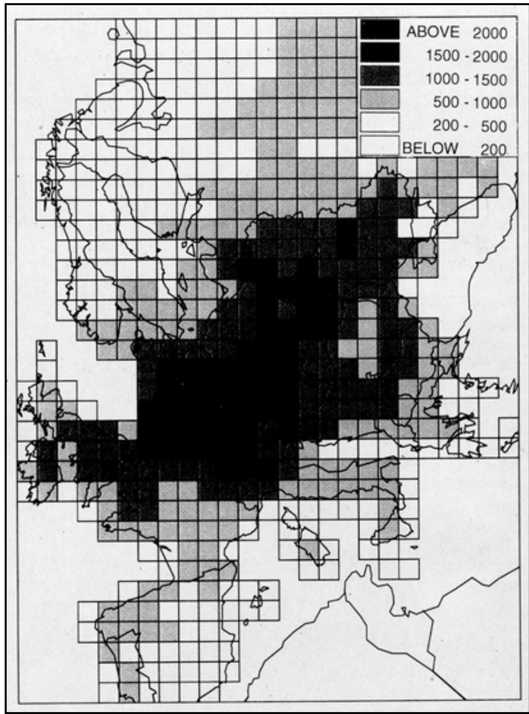
Nitrogen emissions and deposition in Europe



NOx emissions 1994 (tonnes N)

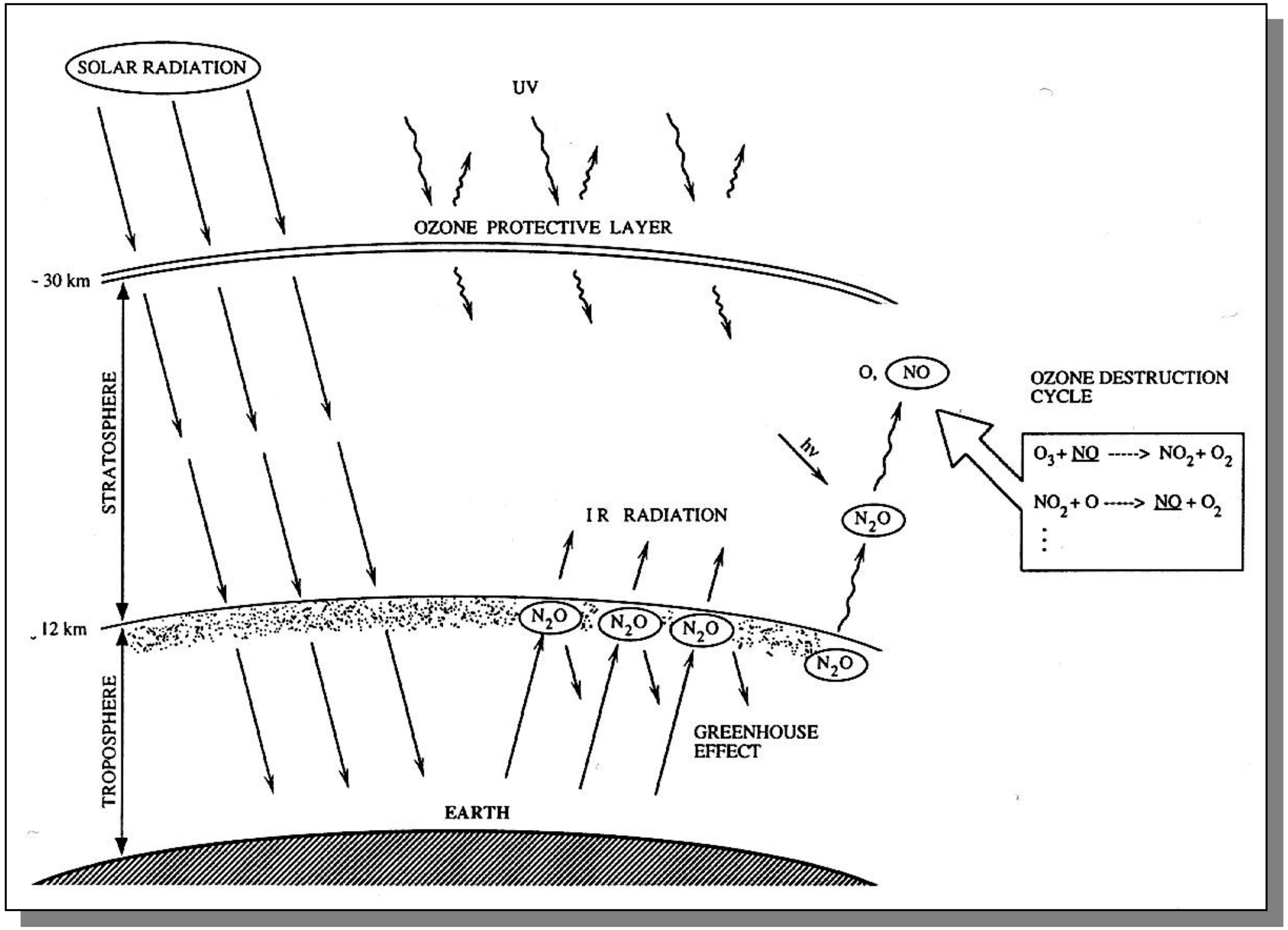


NH_3 emissions 1994 (tonnes N)

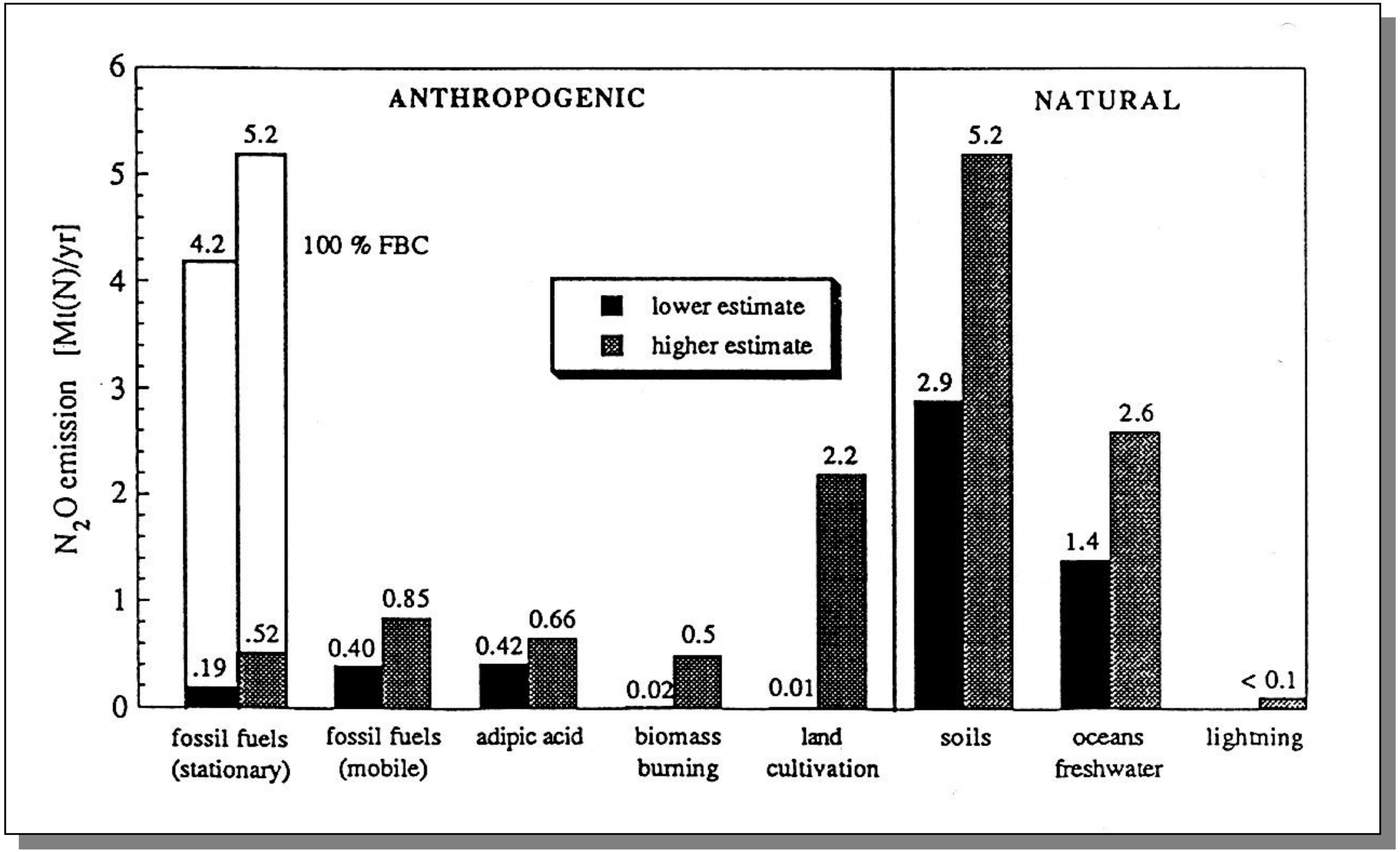


NH_3 + NOdepositions 1994 (mg N/m²)

N_2O as greenhouse gas and in ozone layer depletion



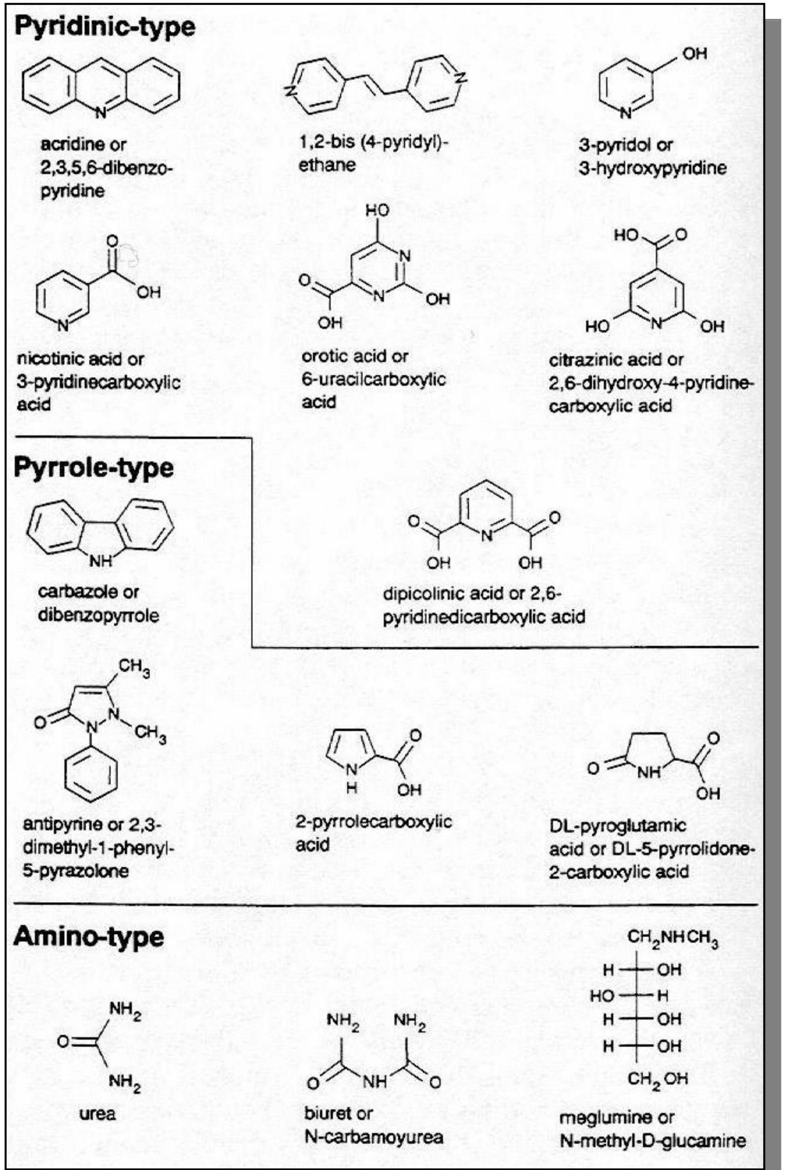
Global sources of N_2O



Emissions of nitrogen compounds and human activities

Sources for NOx	Traffic	~60 %
	Fossil fuel-fired heat and power	~30 %
	Industry	~10 %
Sources for NH_3	Agriculture	~80 %
Sources for N_2O	Fossil fuel-fired heat and power	~30 %
	Forest fires, landgain, …...	~60 %
	Industry (*e.g.* adipic acid production)	~10 %

Nitrogen-containing structures in solid fossil fuels and biomass



	C	H	N	O	O/N atomic ratio
Acridine	87.1	5.1	7.8	–	–
1,2-Bis(4-pyridyl)ethane	78.3	6.5	15.2	–	–
3-Pyridol	63.2	5.3	14.7	16.8	1.1
Nicotinic acid	58.5	4.1	11.4	26.0	2.3
Orotic acid	38.5	2.6	17.9	41.0	2.3
Citrazinic acid	46.5	3.2	9.0	41.3	4.6
Dipicolinic acid	50.3	3.0	8.4	38.3	4.6
Carbazole	86.2	5.4	8.4	–	–
Antipyrine	70.2	6.4	14.9	8.5	0.6
2-Pyrrolecarboxylic acid	54.1	4.5	12.6	28.8	2.3
DL-Pyroglutamic acid	46.5	5.4	10.9	37.2	3.4
Urea	20.0	6.7	46.7	26.6	0.6
Biuret	23.3	4.9	40.7	31.1	0.8
Meglumine	43.5	7.8	7.3	41.4	5.7

Nitrogen in of fuels (dry %-wt)

Fossil fuels		Biomasses & waste -	derived fuels
Coal	0.5 – 3	Wood	0.1 – 0.5
		Bark	~ 0.5
Oil	< 1	Straw	0.5 – 1
Natural gas	0.5 – 20		
Light fuel oil	~ 0.2	Sewage sludge	~ 1
Heavy fuel oil	~ 0.5	Car tyre scrap	~ 0.3
		Municipal solid waste (MSW)	1 – 5
Peat	1 – 2	Refuse derived fuel (RDF)	~ 1
		Packaging derived fuel (PDF)	~ 1
Petroleum coke	~ 3	Auto shredder residue (ASR)	~ 0.5
		Leather waste	~ 12
Orimulsion™	~ 4	Black liquor solids	0.1 - 0.2

NOx (NO_2) emission standards for EU

Solid Fuels

(directive 2001/80/EC)

Fuel	New / Existing*	Plant size (MW_{th})	Emission standard (mg/m^3_{STP} dry)	Comments
Solid**	Existing	50 - 500	600 @ 6% O_2	
"	"	> 500	500 @ 6% O_2	Until 1.1.2016; if after 1.1.2008 < 2000 h/y then 600 @ 6% O_2
"	"	> 500	200 @ 6% O_2	After 1.1.2016; if < 1500 h/y then 450 @ 6% O_2
Solid, general	New	50 - 100	400 @ 6% O_2	
"	"	100 – 300	200@ 6% O_2	"Outermost regions" 300 @ 6% O_2
"	"	> 300	200 @ 6% O_2	
Solid, biomass	New	50 - 100	400 @ 6% O_2	
"	"	100 – 300	200@ 6% O_2	
"	"	> 300	200 @ 6% O_2	

* Existing = plant existing on Nov. 27, 2002 ; or license for new plant requested before that date and plant entering operation before Nov. 27, 2003

** Plants that operated during year 2000 on solid fuels with a volatile content less than 10 %-wt follow a limit of 1200 mg/m^3_{STP} dry @ 6% O_2 until 1.1.2018

*** Applies only to > 70 % load and > 500 h/y operation. Limit is 75 mg/m^3_{STP} dry @ 15 % O_2 for CHP plants > 75 % overall efficiency; combined cycle plants > 55 % electrical efficiency, or mechanical drives. Other, single cycle gas turbines, with efficiency η > 35 % follow the limit value 50× η/35 mg/m^3_{STP} dry @ 15 % O_2

Fuel	New / Existing*	Plant size (MW_{th})	Emission standard (mg/m^3_{STP} dry)	Comments
Liquid	Existing	50 - 500	450 @ 3% O_2	
"	"	> 500	400 @ 3% O_2	
Liquid	New	50 – 100	400 @ 3% O_2	
"	"	100 – 300	200 @ 3% O_2	"Outermost regions" 300 @ 6% O_2
"	"	> 300	200 @ 3% O_2	
Liquid	New	> 50	120 @ 15 % O_2	Gas turbines ***
Gas	Existing	50 - 500	300 @ 3% O_2	
"	"	> 500	200 @ 3% O_2	
Gas, natural	New	50 – 300	150 @ 3% O_2	
"	"	> 300	100 @ 3% O_2	
Gas, other	New	50 – 300	200 @ 3% O_2	
"	"	> 300	200 @ 3% O_2	
Natural gas	New	> 50	50 @ 15 % O_2	Gas turbines ***
Other gas	New	> 50	120 @ 15 % O_2	Gas turbines ***

* Existing = plant existing on Nov. 27, 2002 ; or license for new plant requested before that date and plant entering operation before Nov. 27, 2003

** Plants that operated during year 2000 on solid fuels with a volatile content less than 10 %-wt follow a limit of 1200 mg/m^3_{STP} dry @ 6% O_2 until 1.1.2018

*** Applies only to > 70 % load and > 500 h/y operation. Limit is 75 mg/m^3_{STP} dry @ 15 % O_2 for CHP plants > 75 % overall efficiency; combined cycle plants > 55 % electrical efficiency, or mechanical drives. Other, single cycle gas turbines, with efficiency η > 35 % follow the limit value $50\times \eta/35$ mg/m^3_{STP} dry @ 15 % O_2

NOx (NO_2) emission standards for EU

Liquid and Gaseous Fuels

(directive 2001/80/EC)

NOx (NO_2) emission standards for waste (co-) firing and cement plants for EU (directive 2000/76/EC)

Type of plant	Plant	Emission standard (mg/m^3_{STP} dry)	Comments
Waste incineration	< 6 t /h	200 @ 10 % O_2 *	Daily average
"	> 6 t /h	400 @ 10 % O_2*	Daily average
Cement, incl. co-firing	All	800 / 500 @ 10 % O_2	Existing / new **
Waste co-firing ***	50 – 100 MW_{th}	$C_{process}$ 400 @ 6 % O_2	Solid fuel
"	"	$C_{process}$ 350 @ 6 % O_2	Biomass
"	"	$C_{process}$ 400 @ 3 % O_2	Liquid fuel
"	100 – 300 MW_{th}	$C_{process}$ 300 @ 6 % O_2	Solid fuel
"	"	$C_{process}$ 300 @ 6 % O_2	Biomass
"	"	$C_{process}$ 400 @ 3 % O_2	Liquid fuel
"	> 300 MW_{th}	$C_{process}$ 200 @ 6 % O_2	Solid fuel
"	"	$C_{process}$ 300 @ 6 % O_2	Biomass
"	"	$C_{process}$ 400 @ 3 % O_2	Liquid fuel

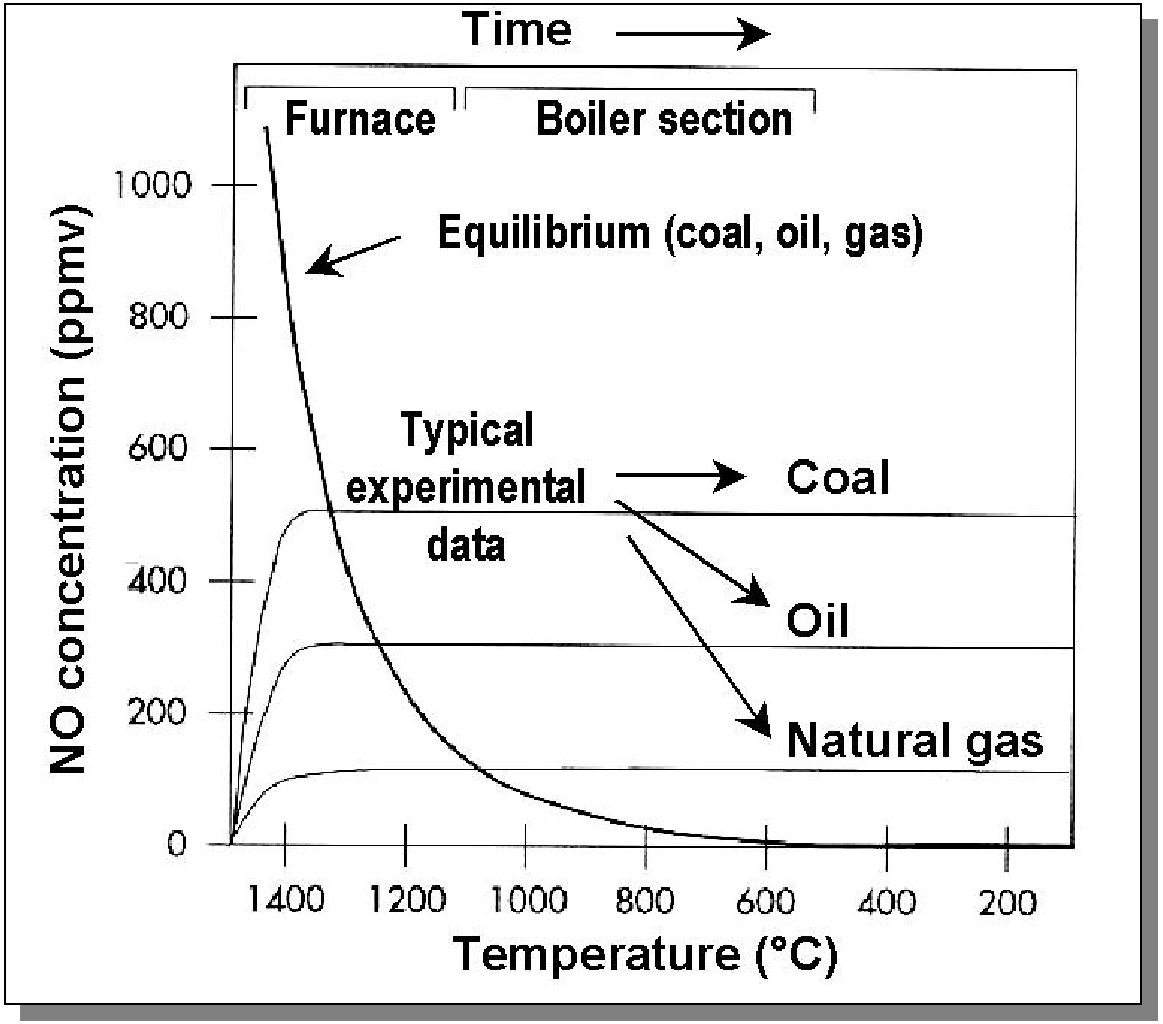
* Various exceptions until 1.1.2008 or 1.1.2010, and until 1.1.2007 these regulations do not apply to hazardous waste incineration

** Existing = plant existing on Dec. 28, 2002; or license for new plant requested before that date and plant entering operation on Dec. 28, 2003 or Dec. 28, 2004. Until 1.1.2008 special regulation 1200 mg/m^3_{STP} dry @ 10 % O_2 for existing wet kilns and small kilns co-firing less than 3 t waste /h.

*** Various exceptions until 1.1.2008 for existing fluidised beds 100 – 300 MW_{th} that burn solid fuels or biomass provided that $C_{process}$ < 350 mg/m^3_{STP} dry @ 6 % O_2. Until 1.1.2007 these regulations do not apply to hazardous waste incineration

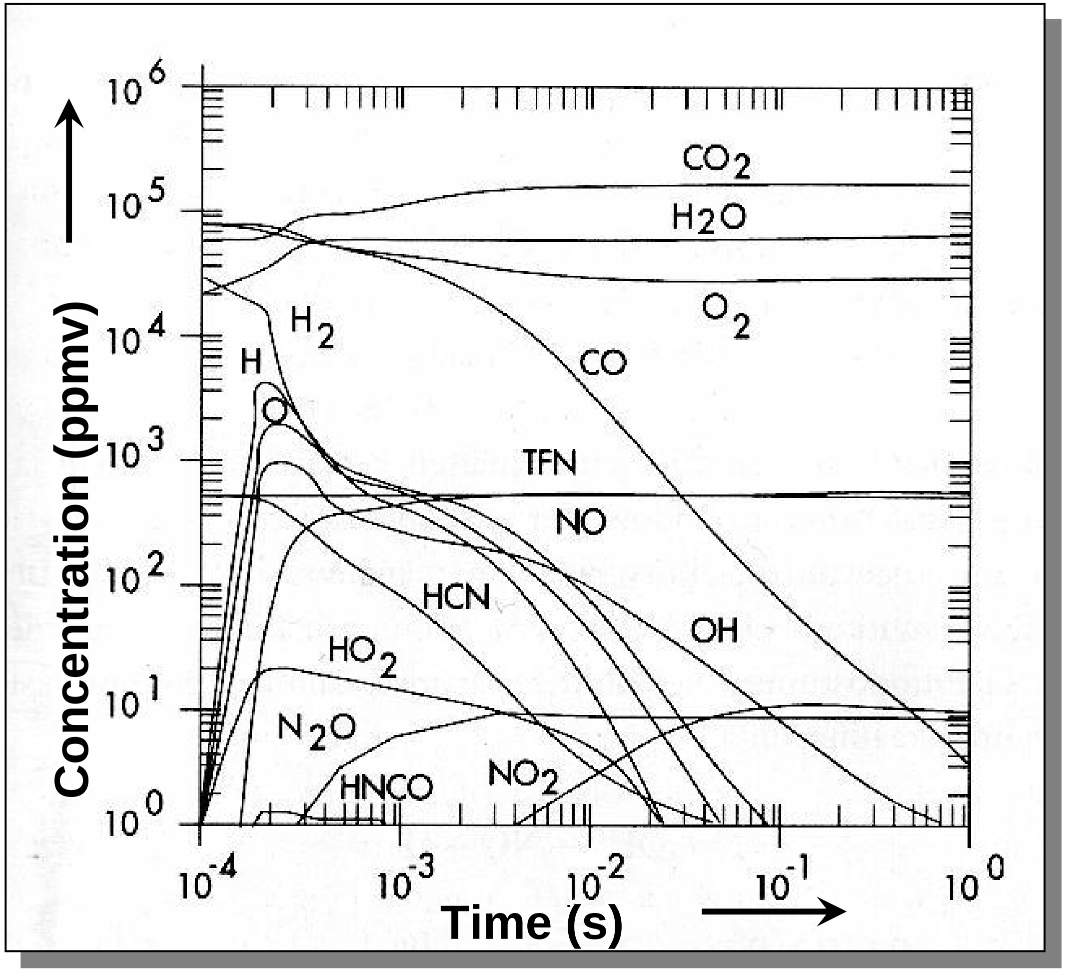
$$C_{co\text{-}firing} = (V_{waste} \cdot C_{waste} + V_{process} \cdot C_{process})/(V_{waste} + V_{process}),\ V = \text{exhaust volume}$$

NO formation in pulverised coal, oil and natural gas firing



Thermodynamics *versus* measurements

Kinetic modelling of coal pyrolysis gas combustion



Combustion in plug flow reactor (PFR).

850°C, 1 bar.

Initial gas (%-vol):

8% CO, 3% H_2, 2% H_2O

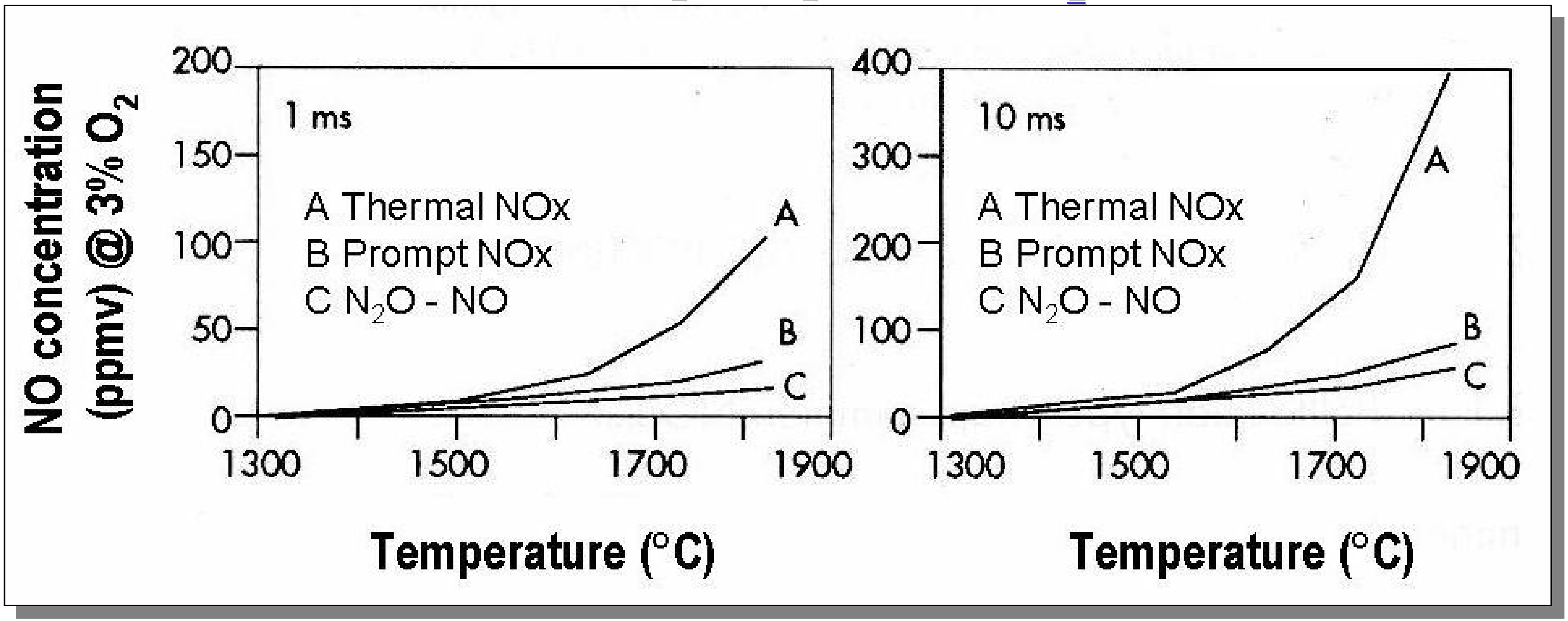
0.05% HCN, 8% O_2, 73%N_2

NO Formation from N_2 Fixation: $N_2 \rightarrow NO$

n:o	Reaction
1	Thermal NO $N_2 + O \rightarrow NO + N$ $N + O_2 \rightarrow NO + O$ $N + OH \rightarrow NO + H$
2	Prompt NO $N_2 + CH \rightarrow HCN + N$ $HCN \xrightarrow{+O} NCO \xrightarrow{+H} NH \xrightarrow{+H} N \xrightarrow{+O_2,+OH} NO$
3	Formation via N_2O intermediate $O + N_2 + M \rightarrow N_2O + M$ $N_2O + O \rightarrow 2NO$

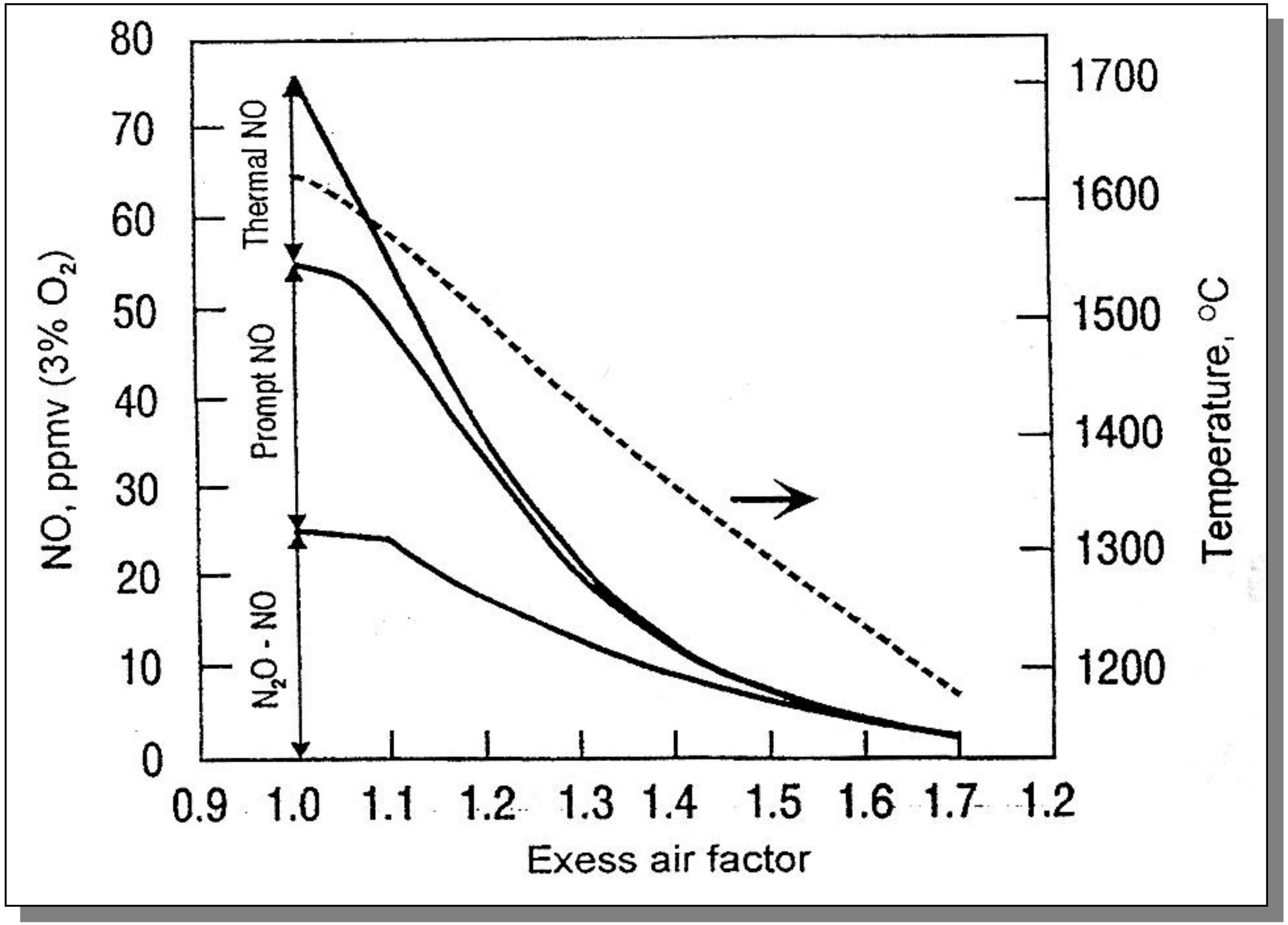
Kinetic modelling of NO formation:

thermal NOx, prompt NOx, N_2O-NO



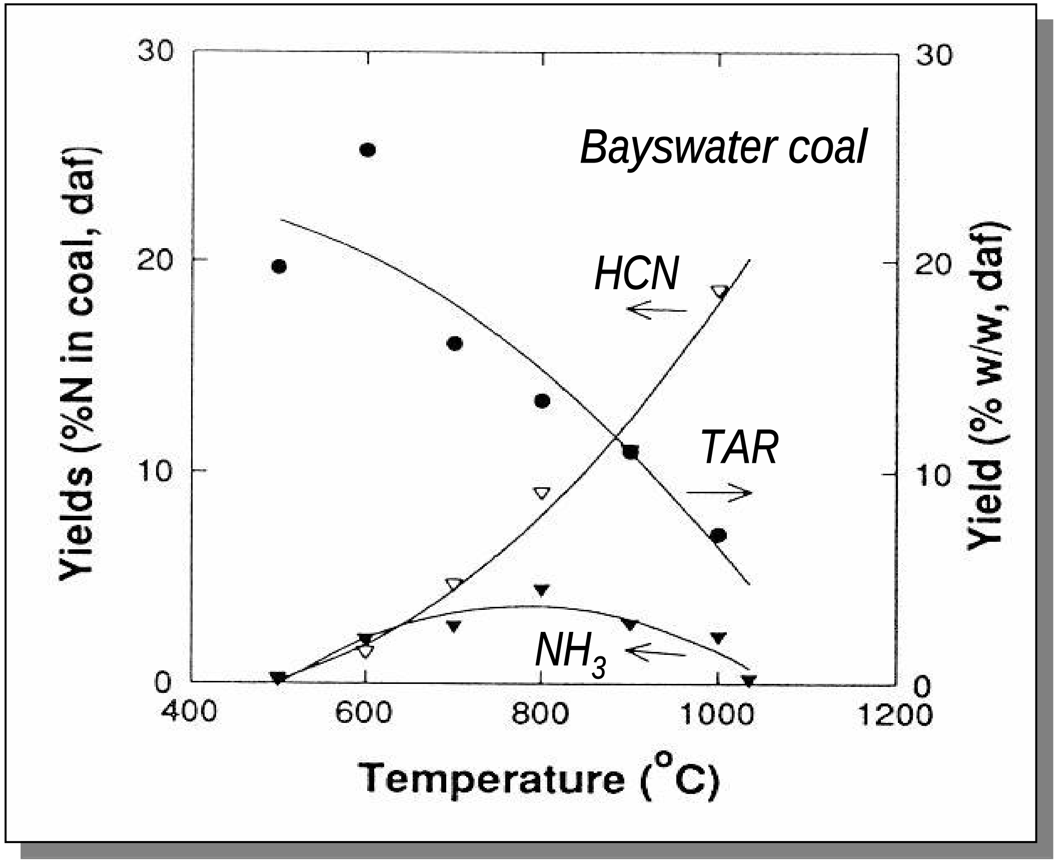
Methane combustion with air in a stirred reactor (CSTR), at 1 bar, air factor $\lambda = 1.15$

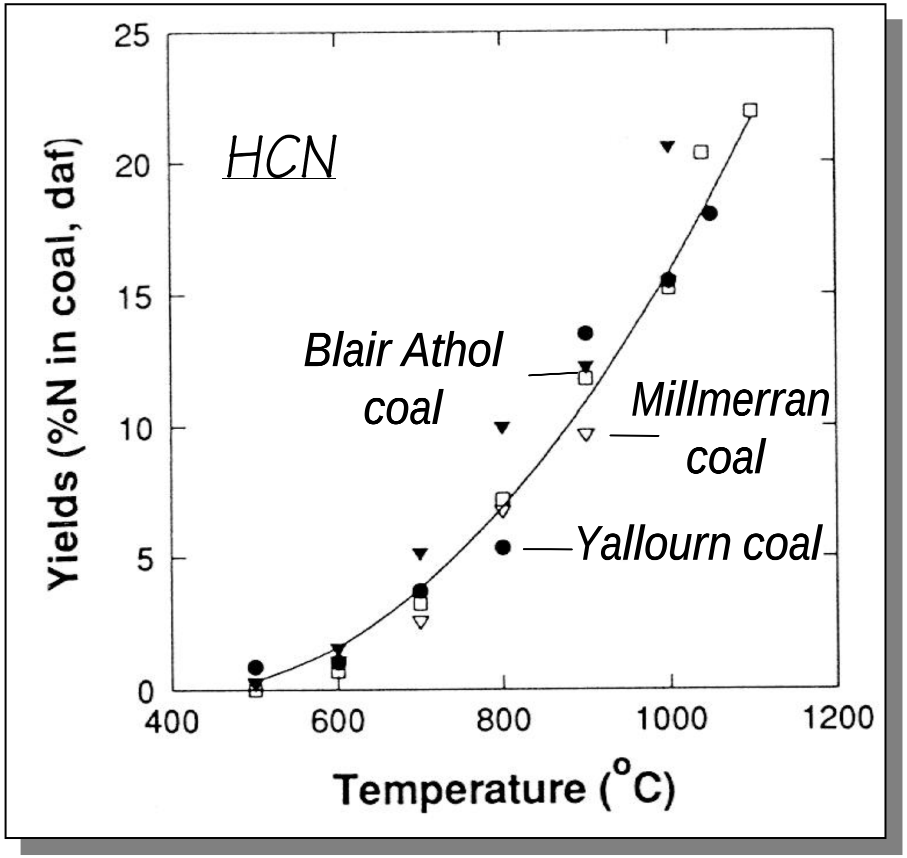
NO formation mechanisms: effect of air factor, λ



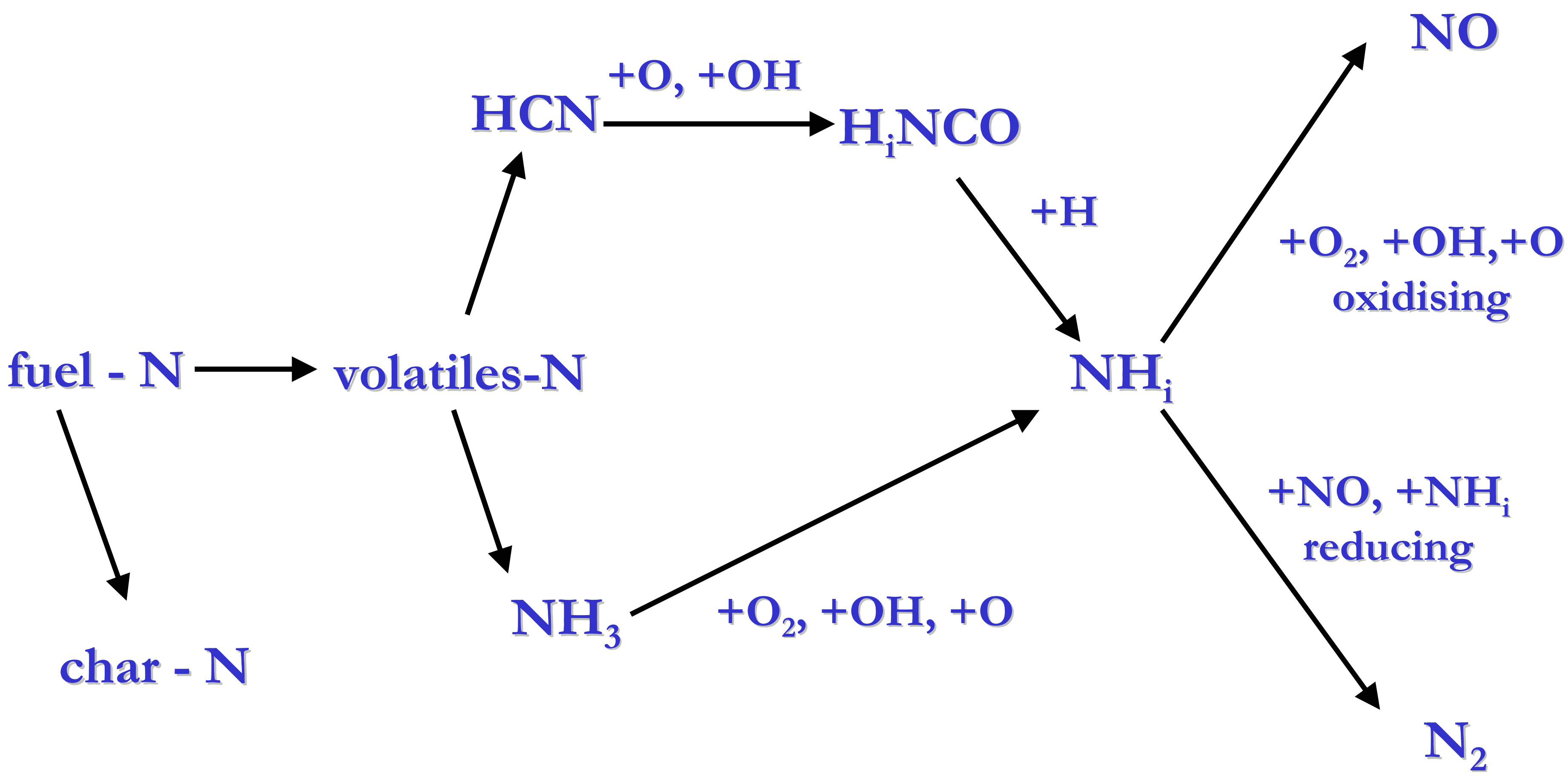
Methane combustion
with air
in a stirred reactor
(CSTR),
at 1 bar,
residence time 4 ms.

Release of Fuel-N during pyrolysis of Australian coal



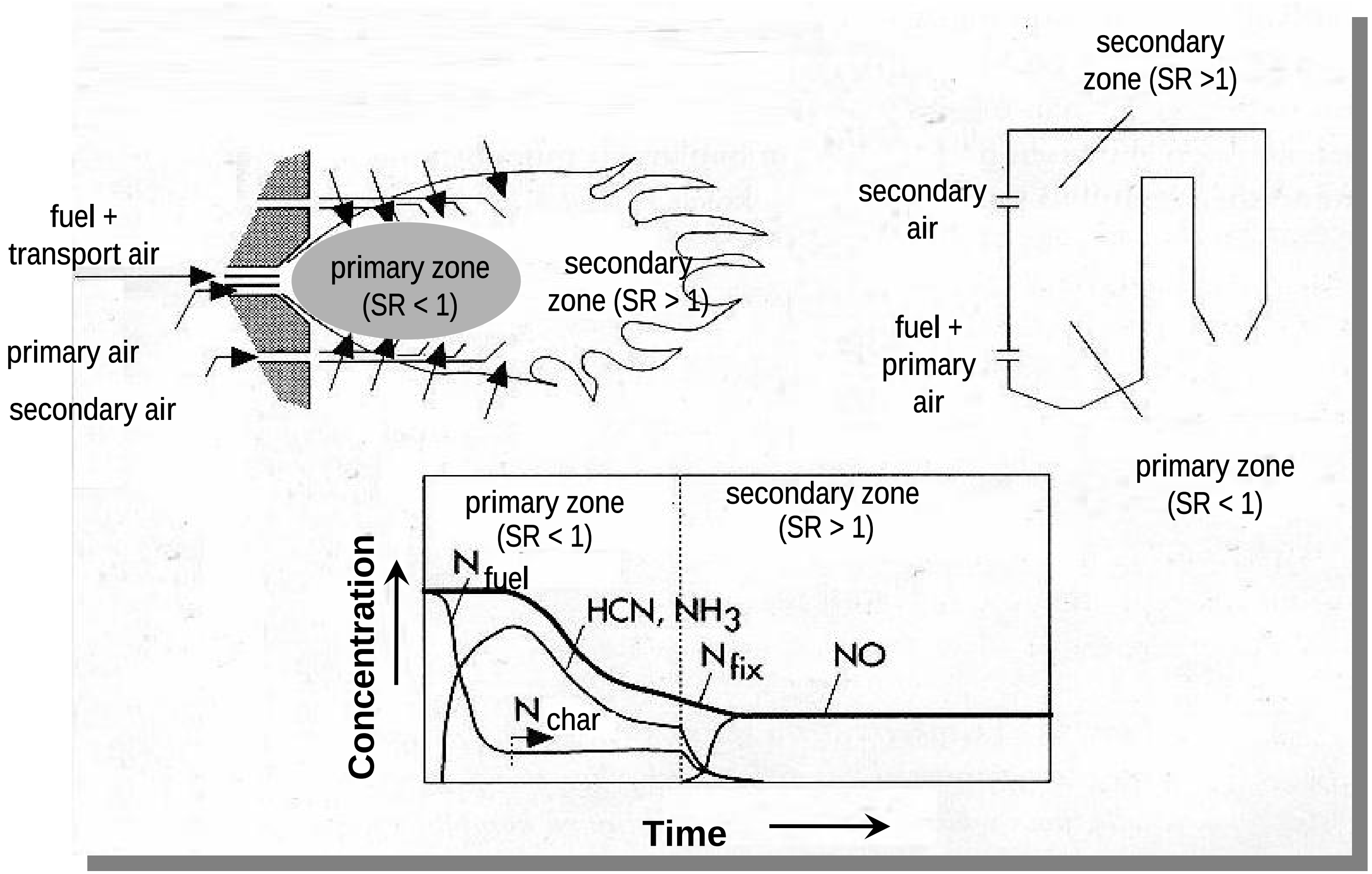


Oxidation of volatile fuel-N compounds during burner combustion (simplified)

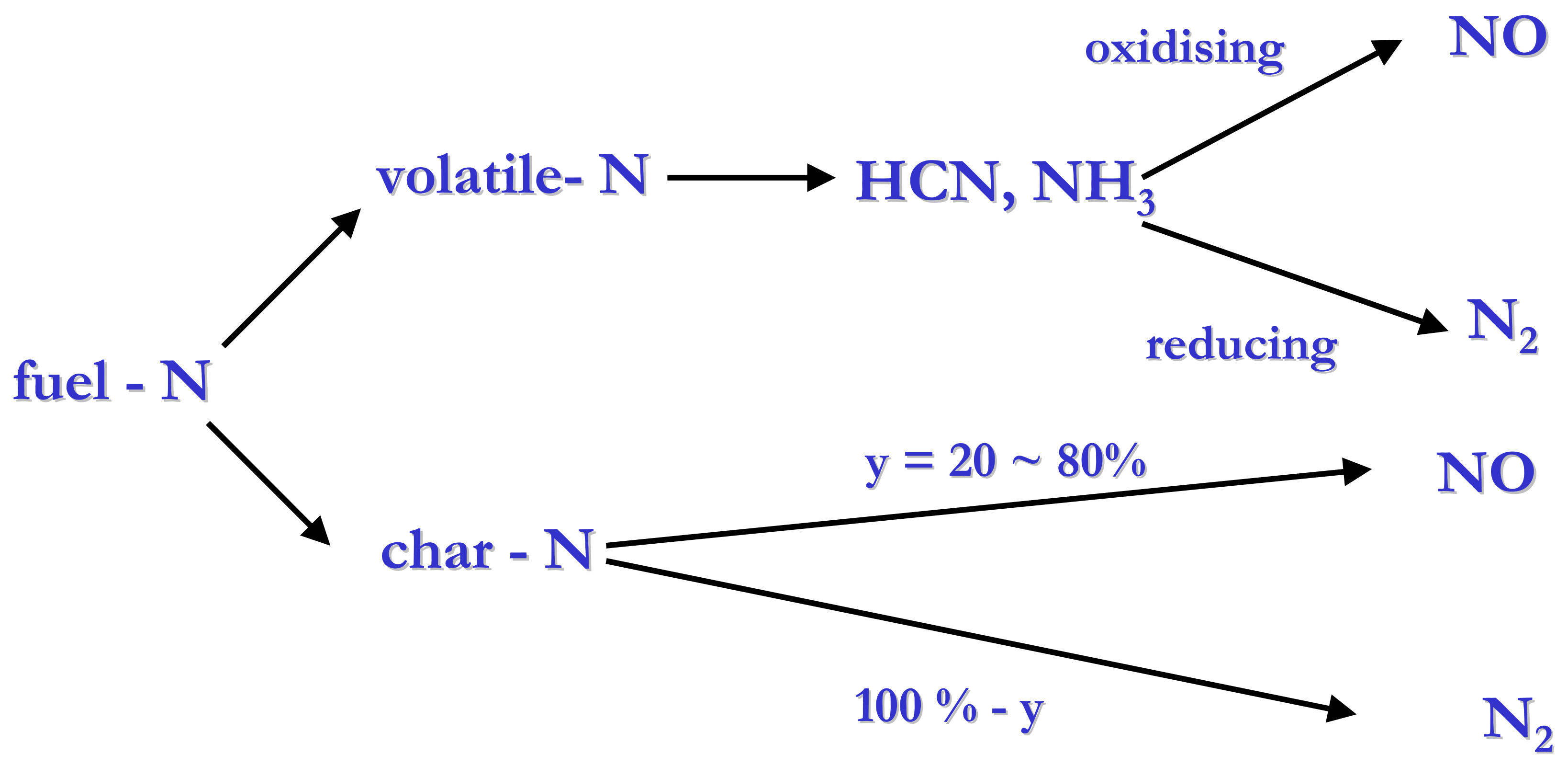


Principle of air staging.

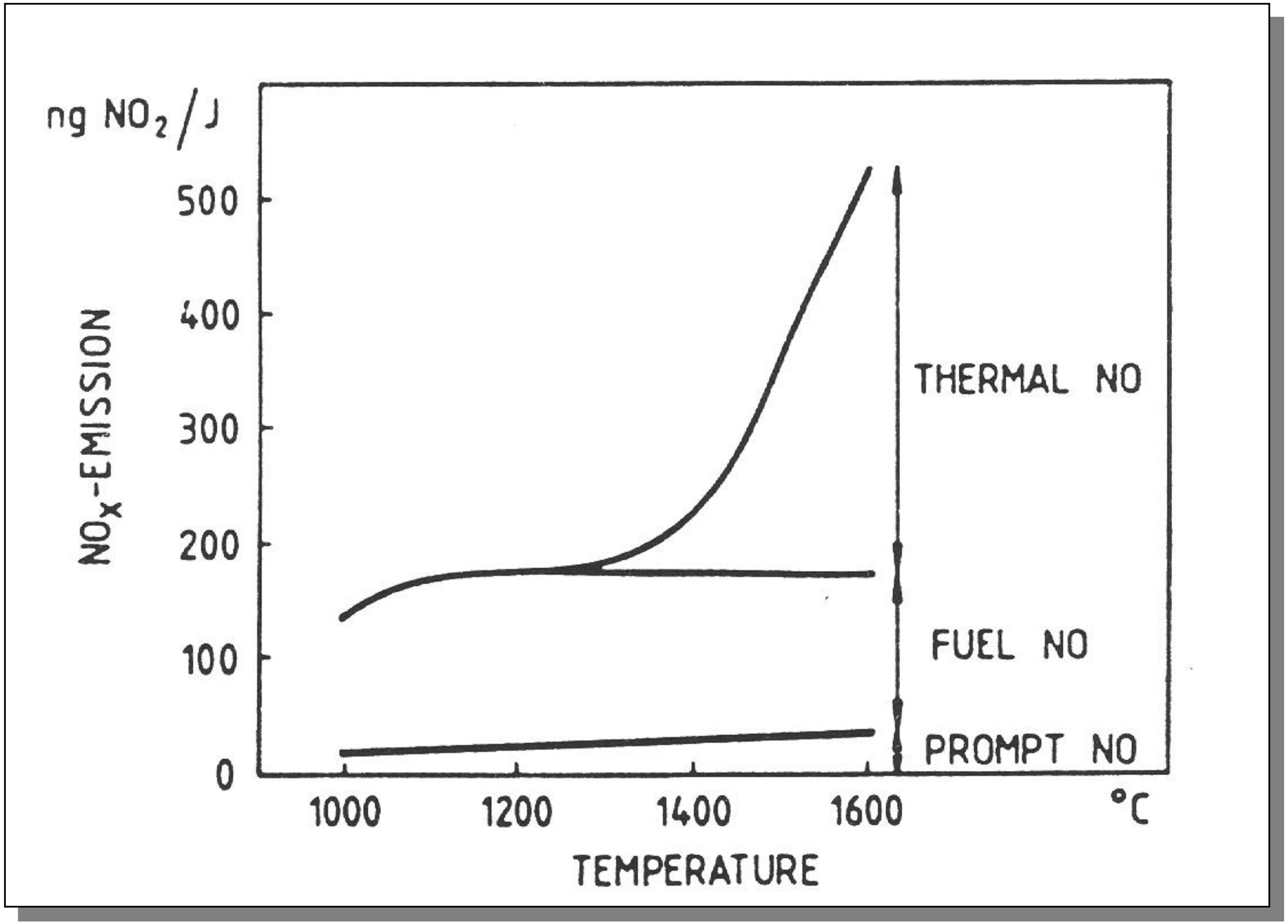
Assumed: char-N gives NO (40%) and N_2 (60%), N_{fix} = all nitrogen compound except N_2



Oxidation of fuel-N to NO and N_2 during burner combustion with significant char-N (simplified)

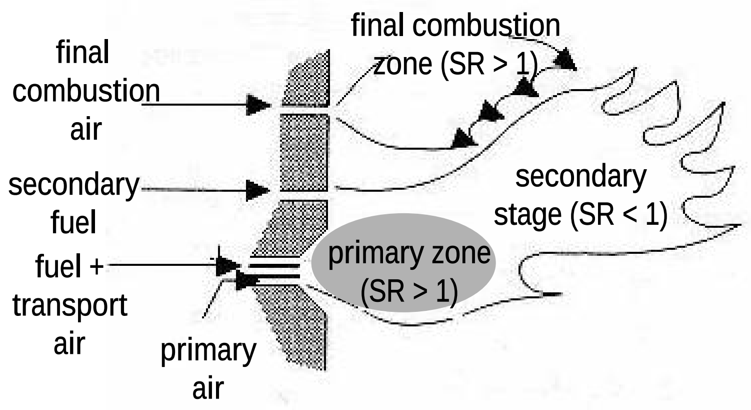


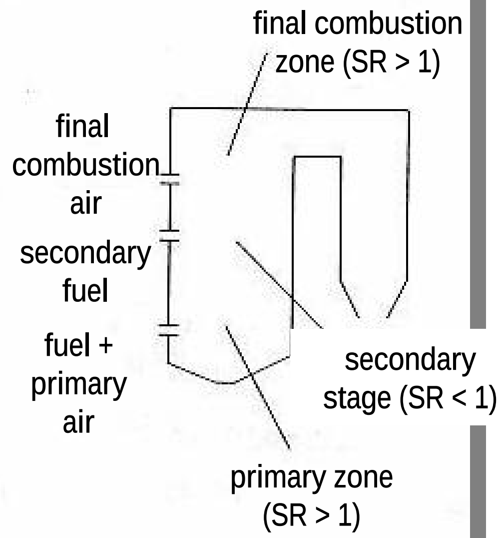
Thermal NOx, prompt NOx, fuel NOx

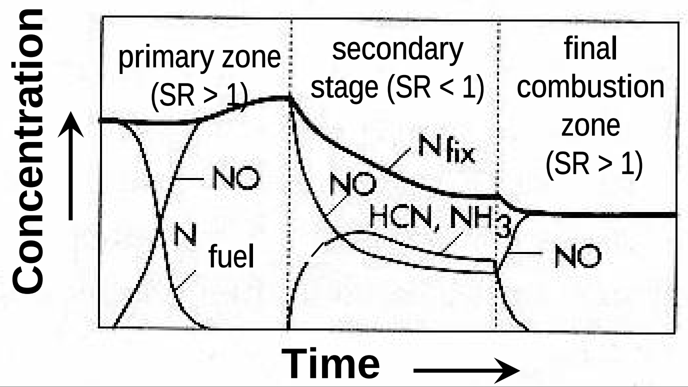


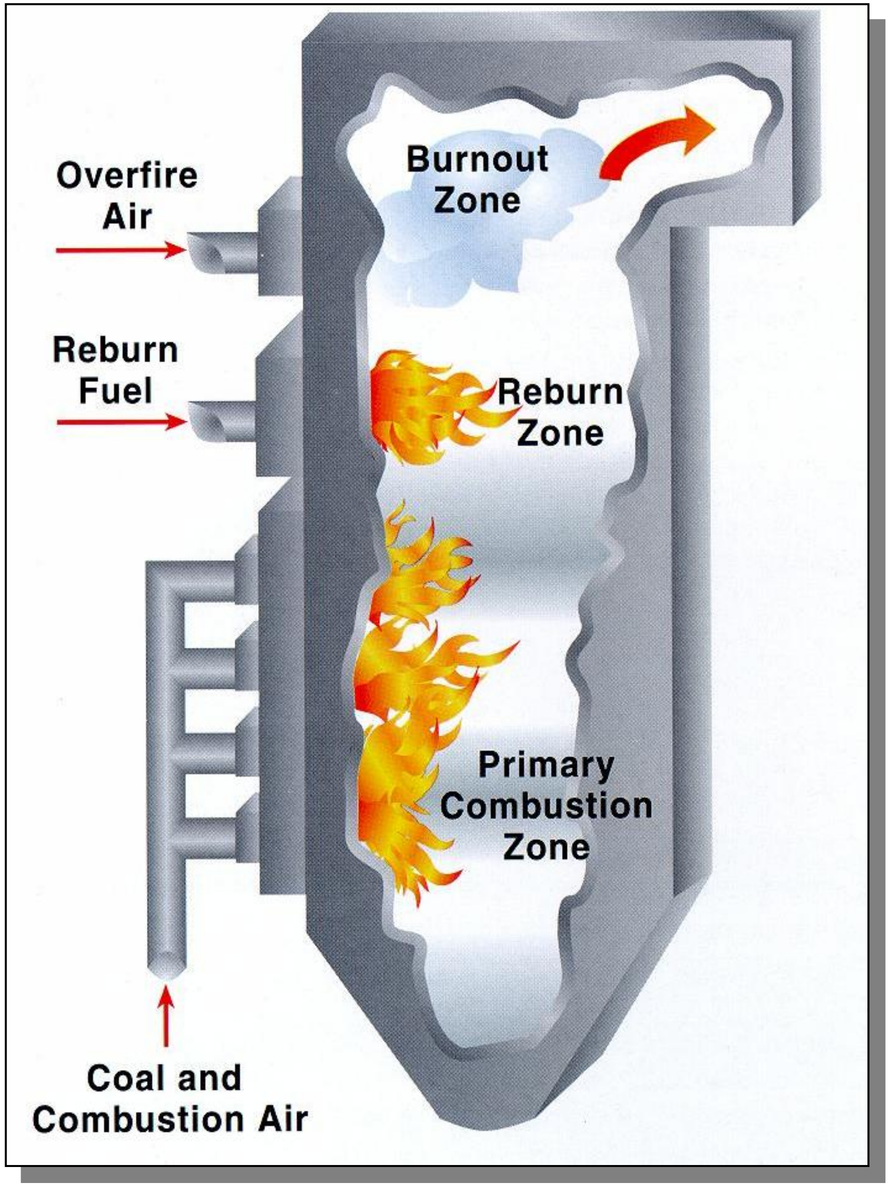
Principle of fuel staging.

Assumed: fuel NO and thermal NO formed during primary stage, N_{fix} = all nitrogen compound except N_2

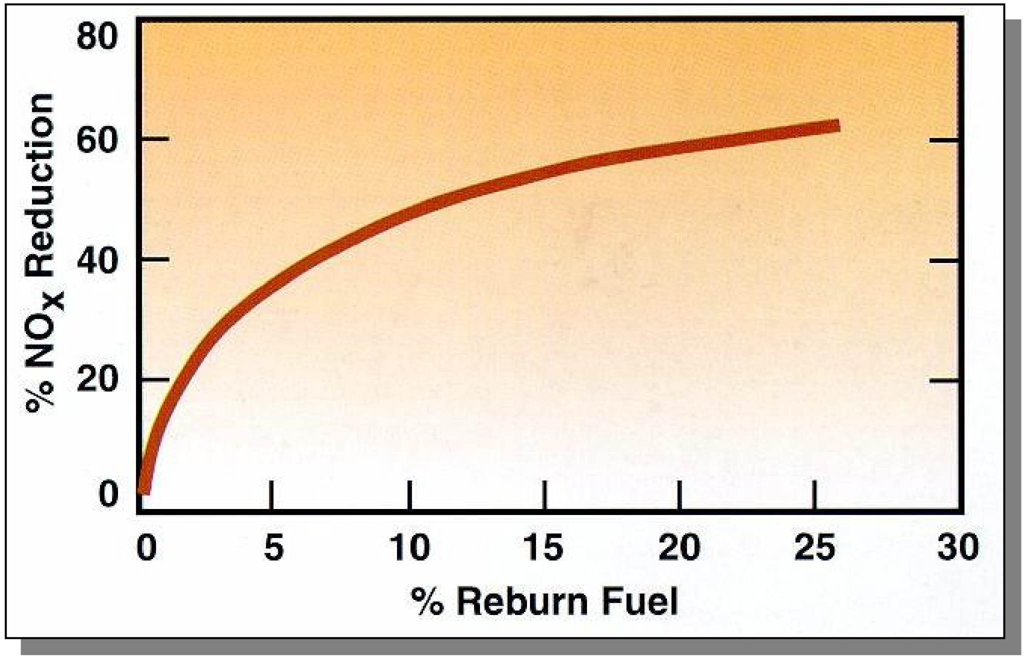




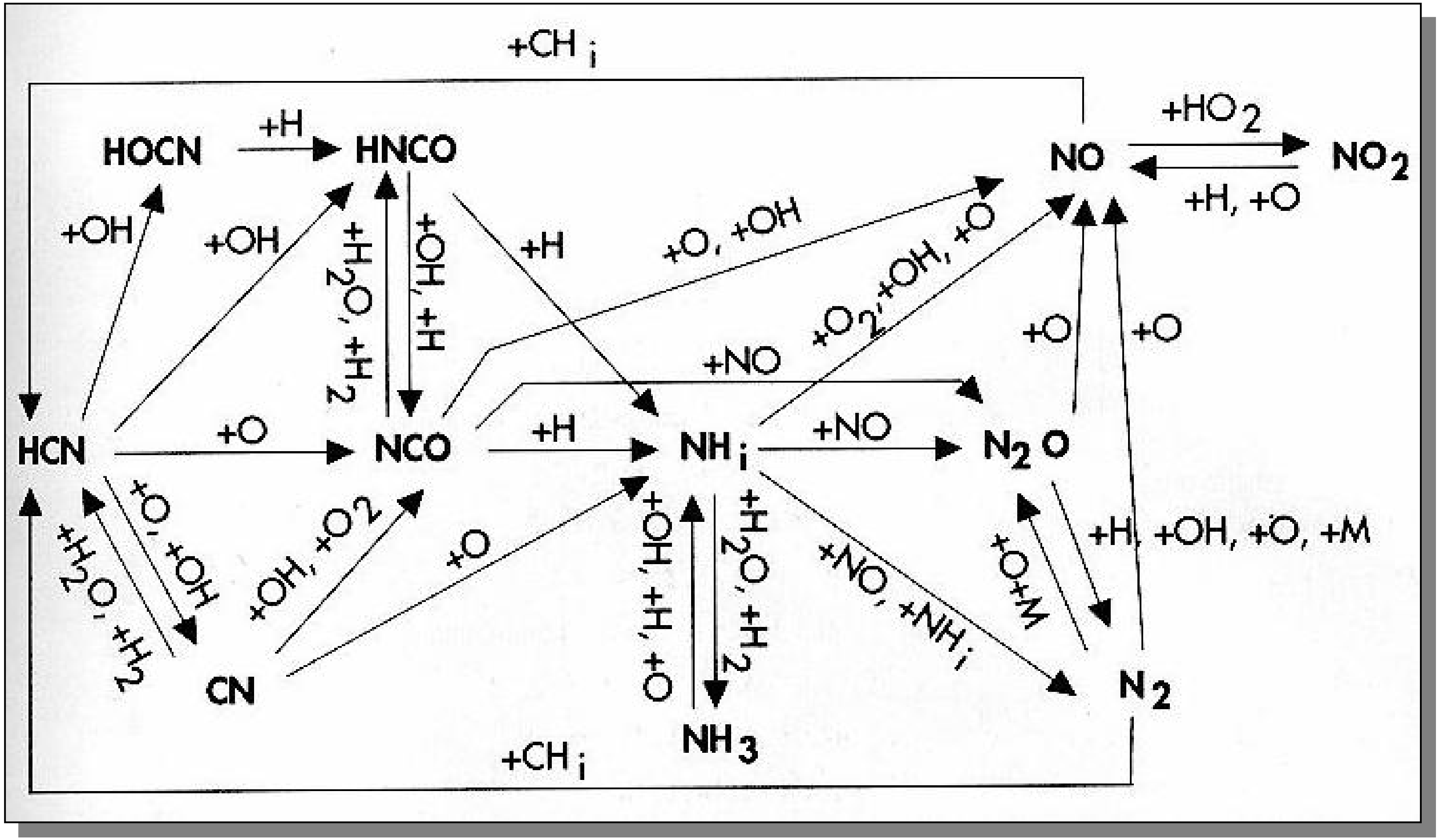




Reburning technology

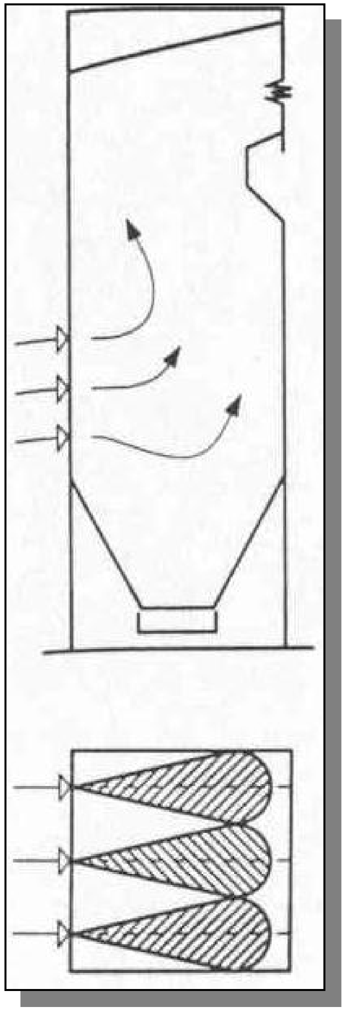


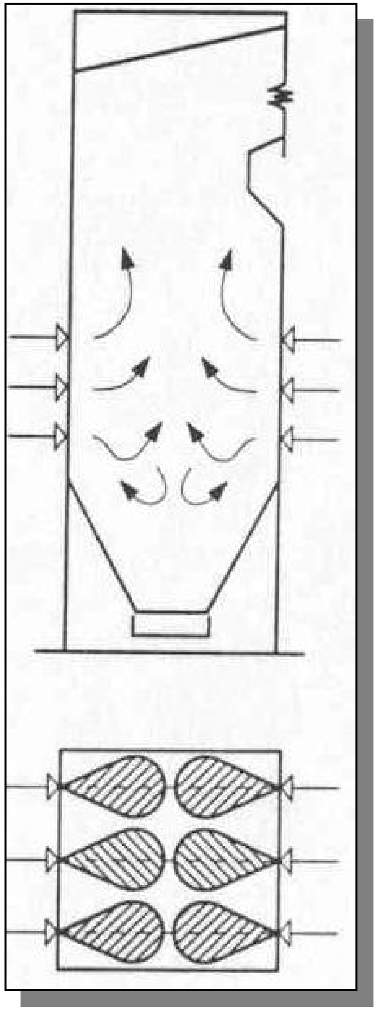
Main NOx formation and decomposition reactions during burner combustion (summary)



Pulverised fuel combustion furnace types

A typical pulverised coal-firing flame





← ←

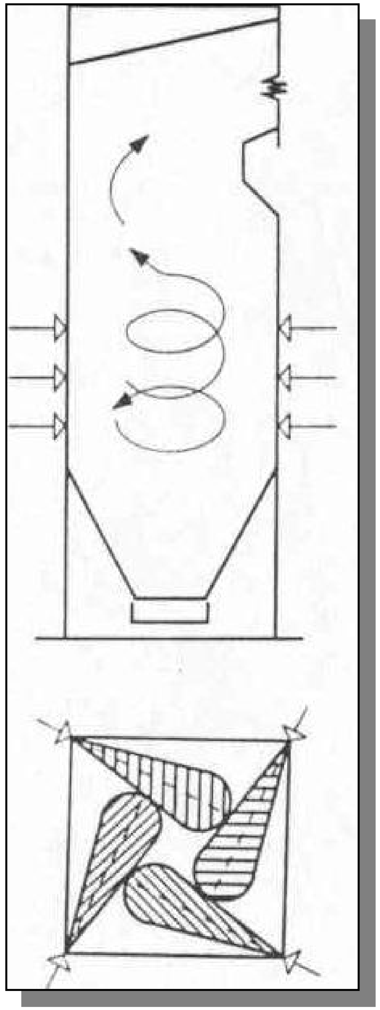
Front wall fired

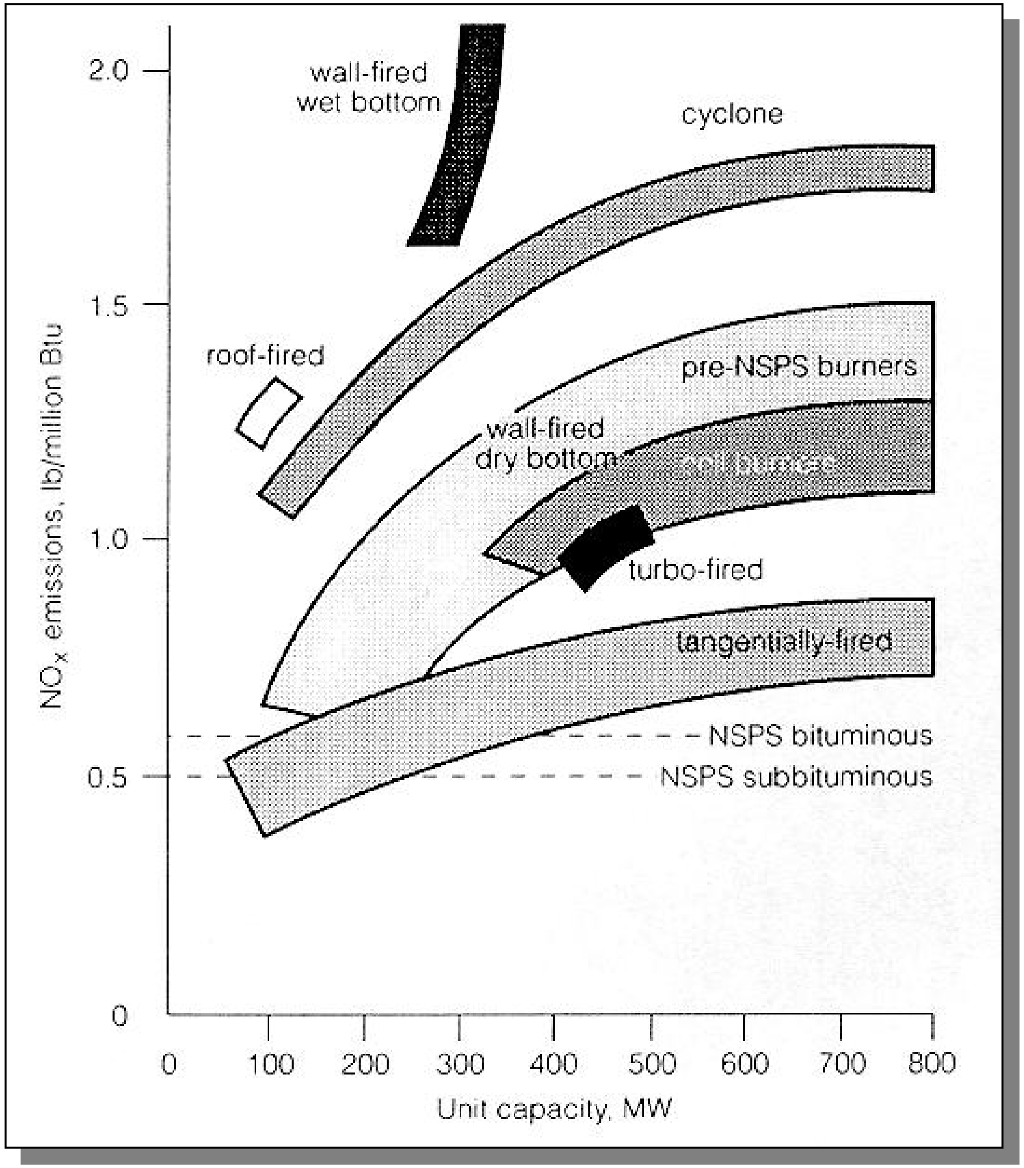
←

Opposed wall fired

→

Tangential / corner fired

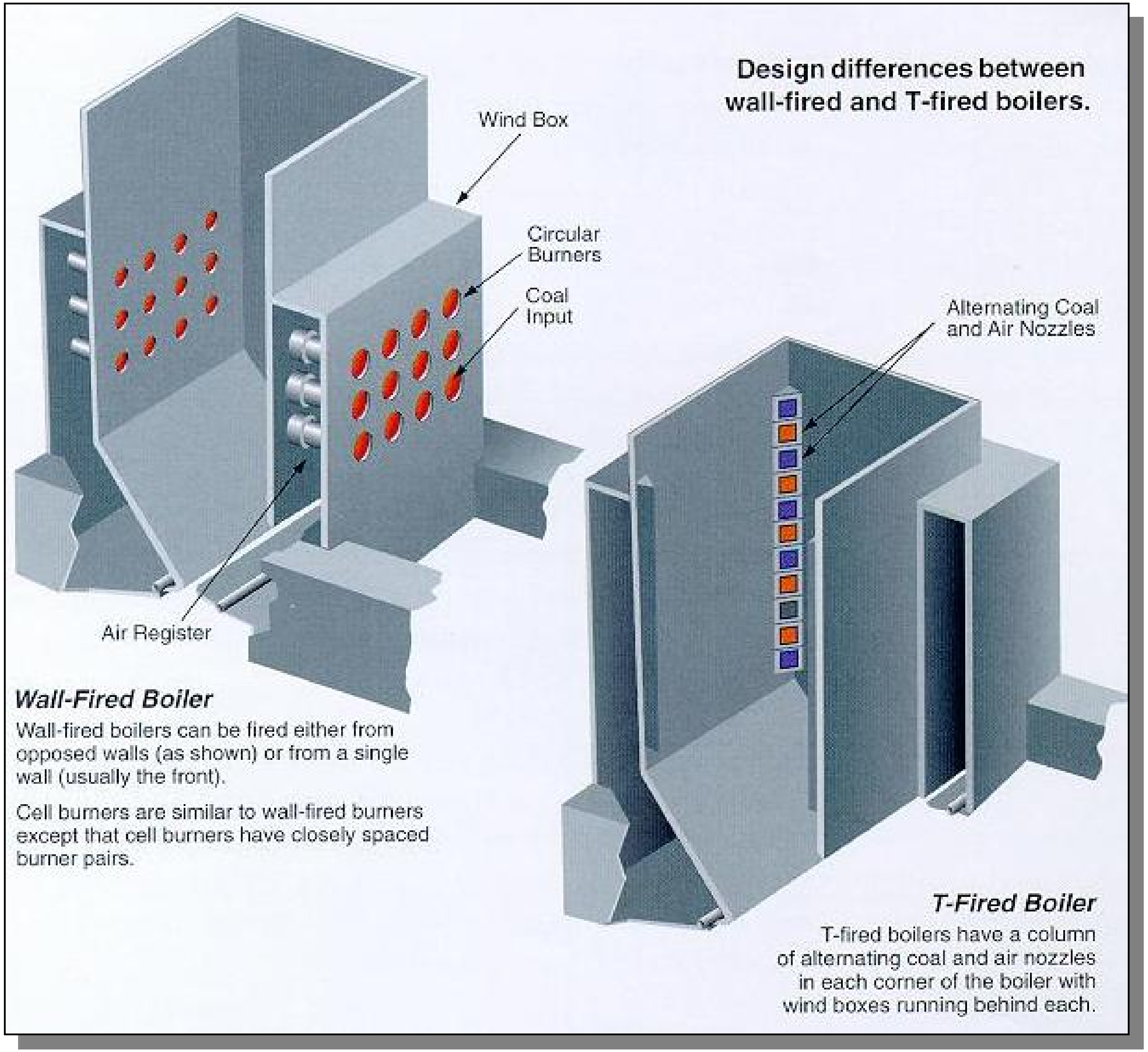




Typical NOx emissions for various types of coal-fired furnaces as function of unit size

Note : 1 lb/MBTU ~ 0.5 mg/GJ

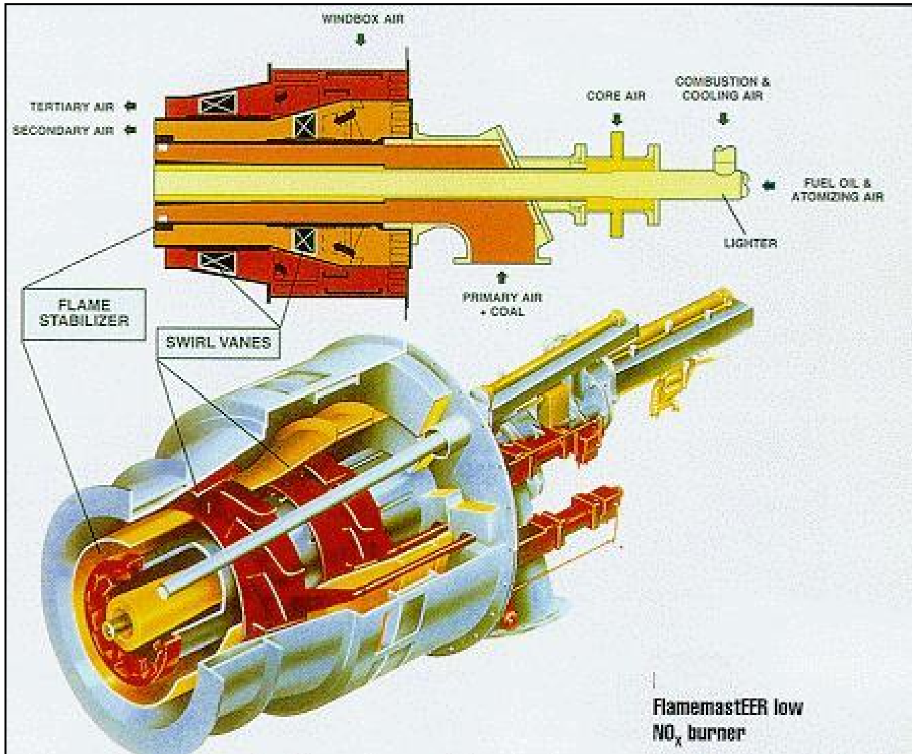
NSPS = New Source Performance Standard



Wall-fired burner combustion and tangential combustion (T-firing)

Low-NOx burners for pulverised coal firing

Tip of low-NOx burner installed on Unit 4 at Arapahoe Station.

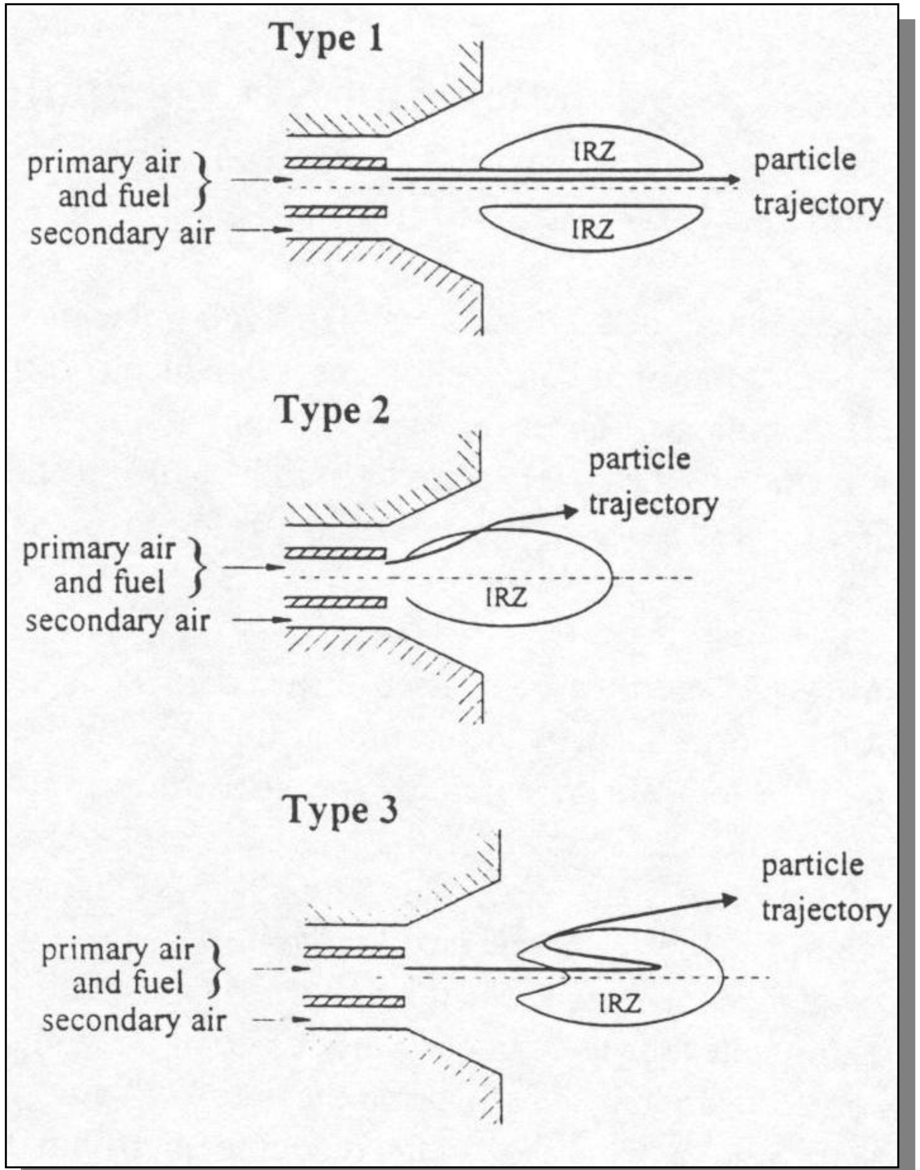


IFRF flame type classification system

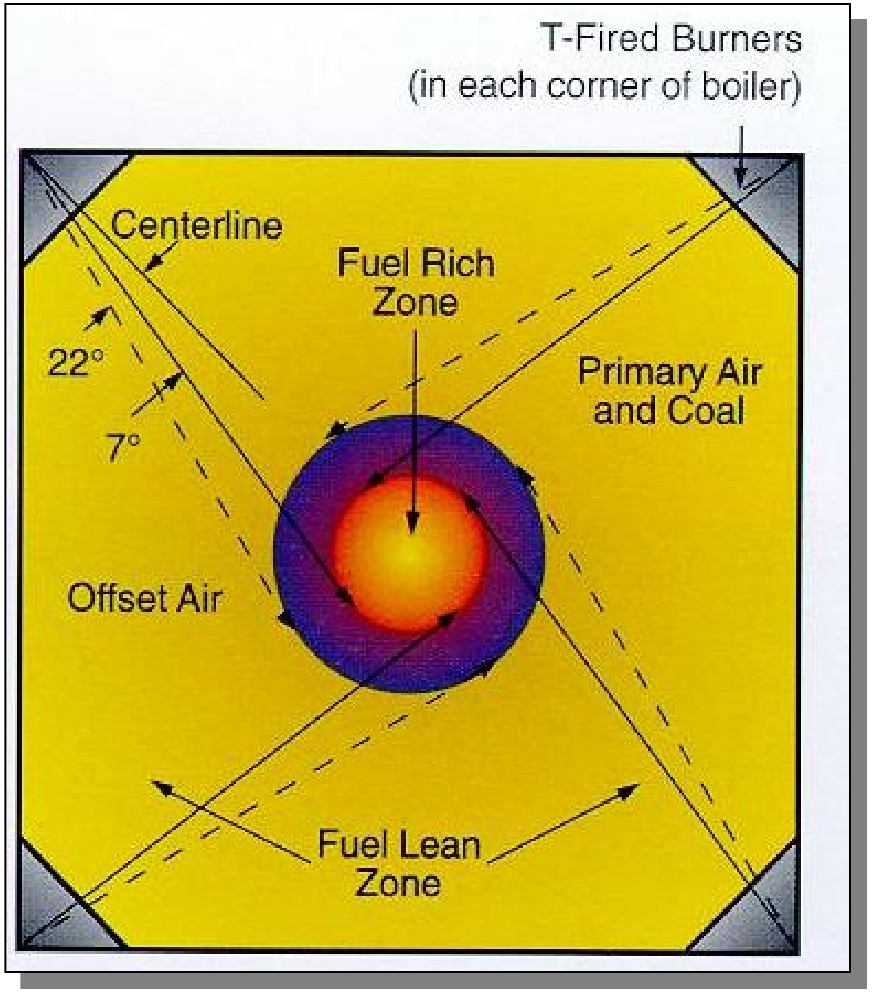
Reverse flow leads to rapid ignition close to the burner, resulting in NO reduction. Sufficient penetration and time in IRZ is crucial !!!!!!

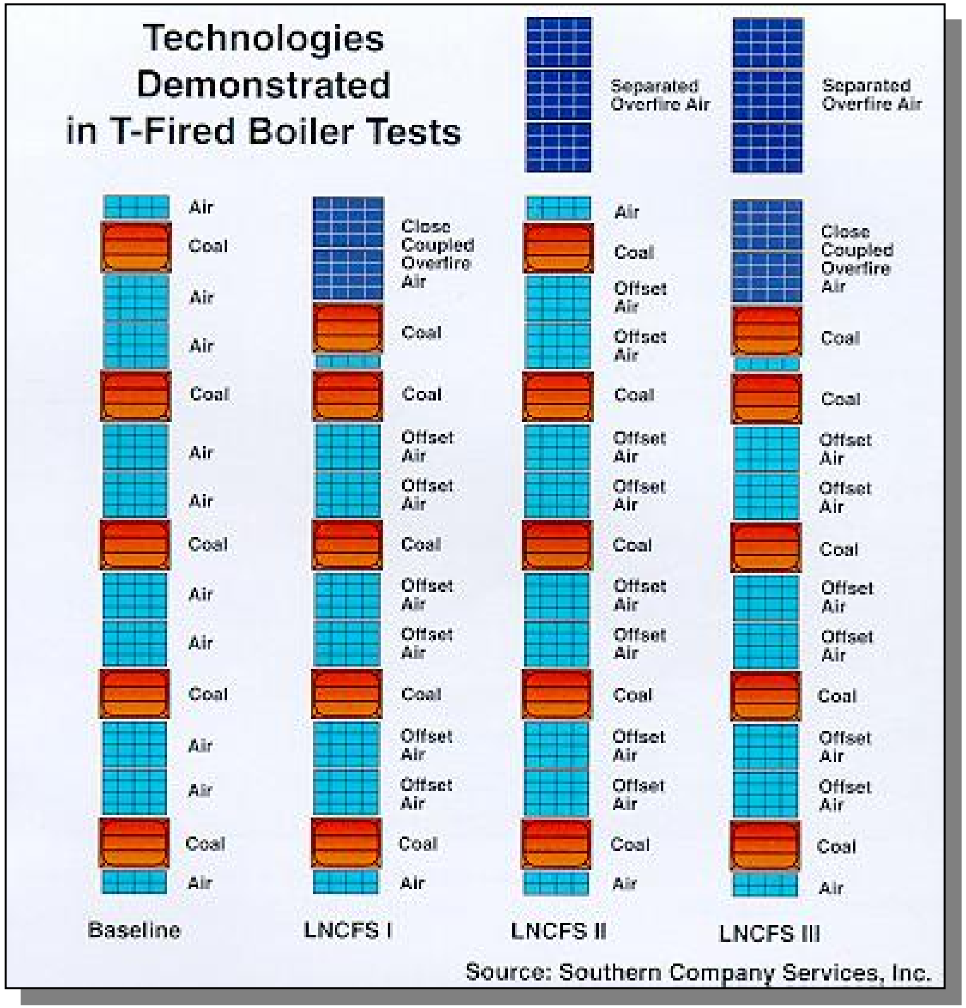
Stoichiometry in primary zone:
λ ~0.6 .. 0.7 is optimal
λ > 0.7 gives more NO
λ < 0.6 gives more NH_3, HCN,... giving more post-flame NO

Stoichiometry ↓ then NO ↓ ,
but carbon-in-ash ↑ and corrosion ↑

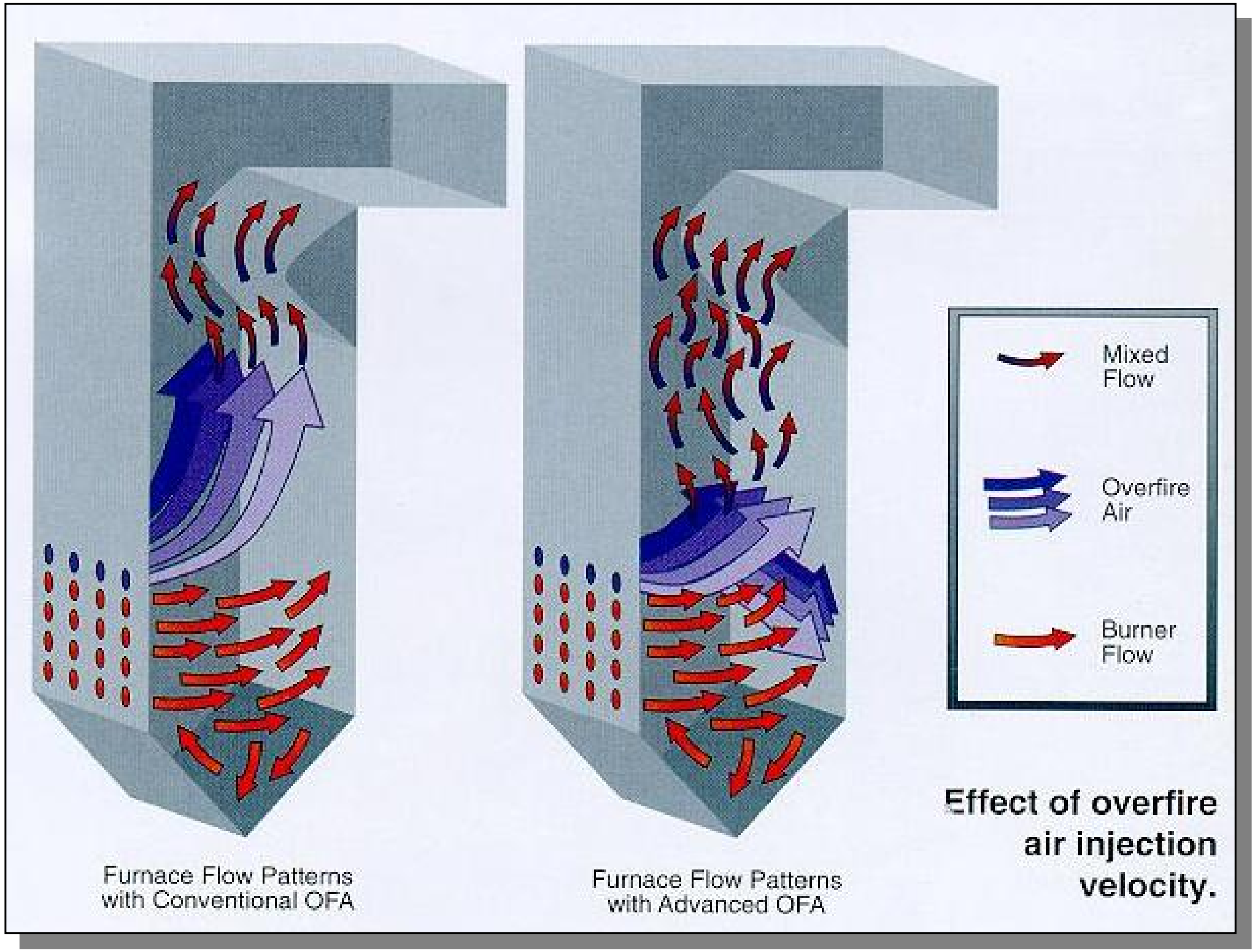


Low-NOx concentric firing system (LCNFS™)

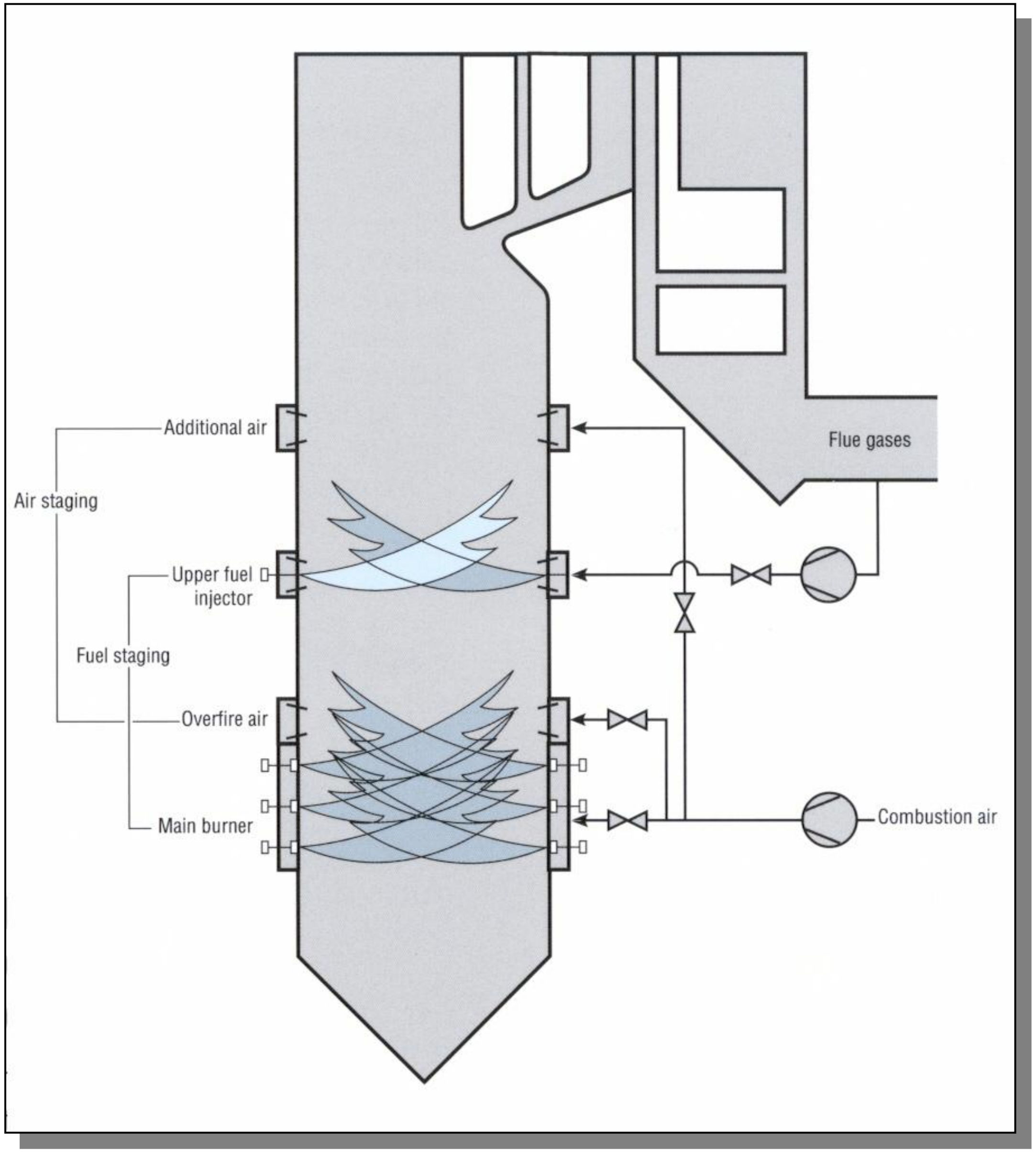


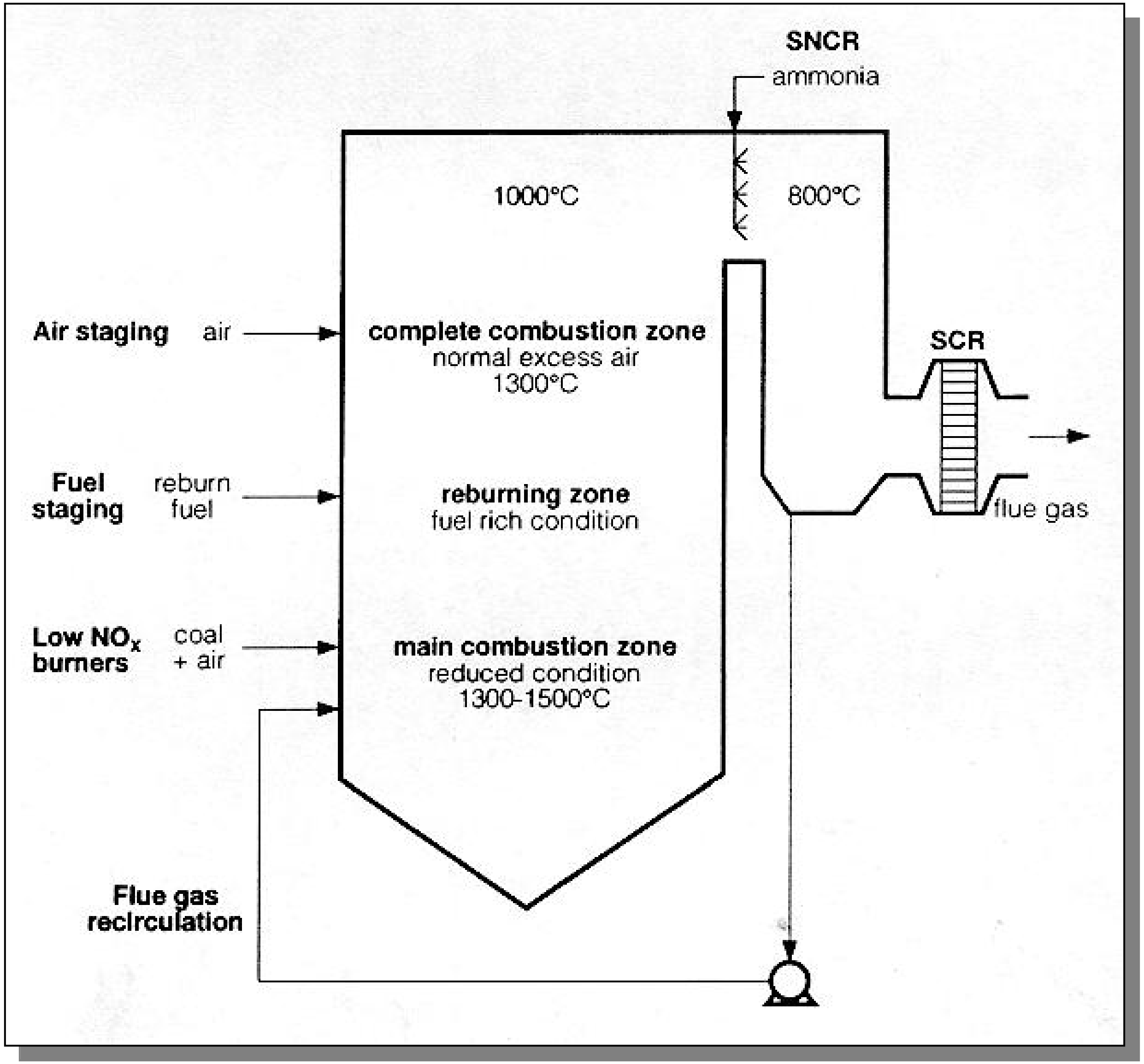


Overfire air (OFA) and advanced OFA



Air and fuel staging for NOx control





Overview of Low-NOx technologies for burner combustion

Overview of Low NOx technologies

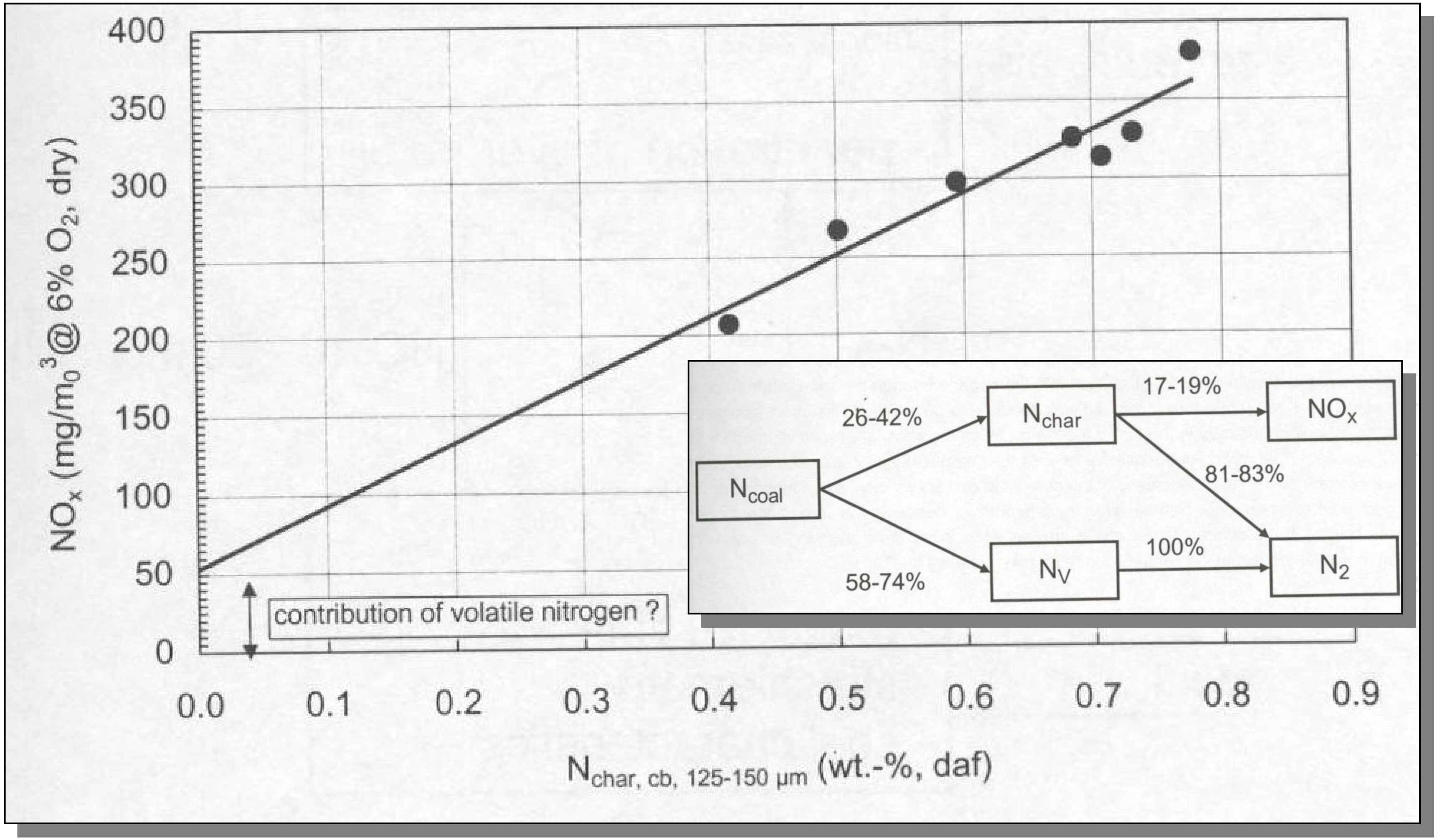
	Advantageous when	Problems
Low excess air	When excess air is used	Fuel burnout decreases
Air staging / over-fire air	In principle always	Limited effect, increased risks for corrosion, fouling, slagging
Low NOx burner *i.e.* in-flame staging	In principle always	Fuel burn-out decreases, not a big problem, however
Fuel staging i.e. reburning with coal, oil, natural gas	In principle always, especially when the reburn fuel is also the start-up fuel	Capital cost of system modifications
Flue gas recirculation	High temperature oil- or gas-fired furnaces	Low efficiency if not combined with other method

Relative effects of Low-NOx technologies

Measures	NO_x emissions, ppmv (6%, O_2)	NO_x reduction, %
Base	550–800	–
Low excess air	450–650	15–20
Low excess air + over fire air	300–500	35–45
Low excess air + flue gas recirculation	350–550	30–35
Low excess air + over fire air + flue gas recirculation	200–400	50–60
Low excess air + over fire air + flue gas recirculation + low NO_x burners	150–300	60–70

NOx emissions model for Hemweg 8 plant

600 MWe, tangential, 1993, 535°C/568°/230 bar (between Amsterdam and Haarlem)



Selective catalytic reduction (SCR) of NOx /1

Chemistry of the SCR Process

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$$

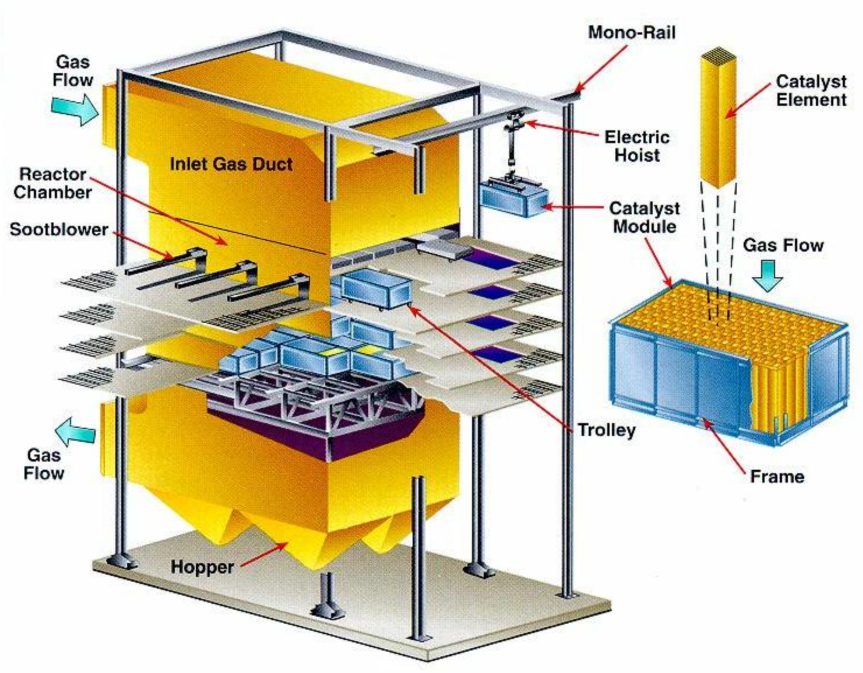
$$2NO_2 + 4NH_3 + O_2 \longrightarrow 3N_2 + 6H_2O$$

Side Reactions

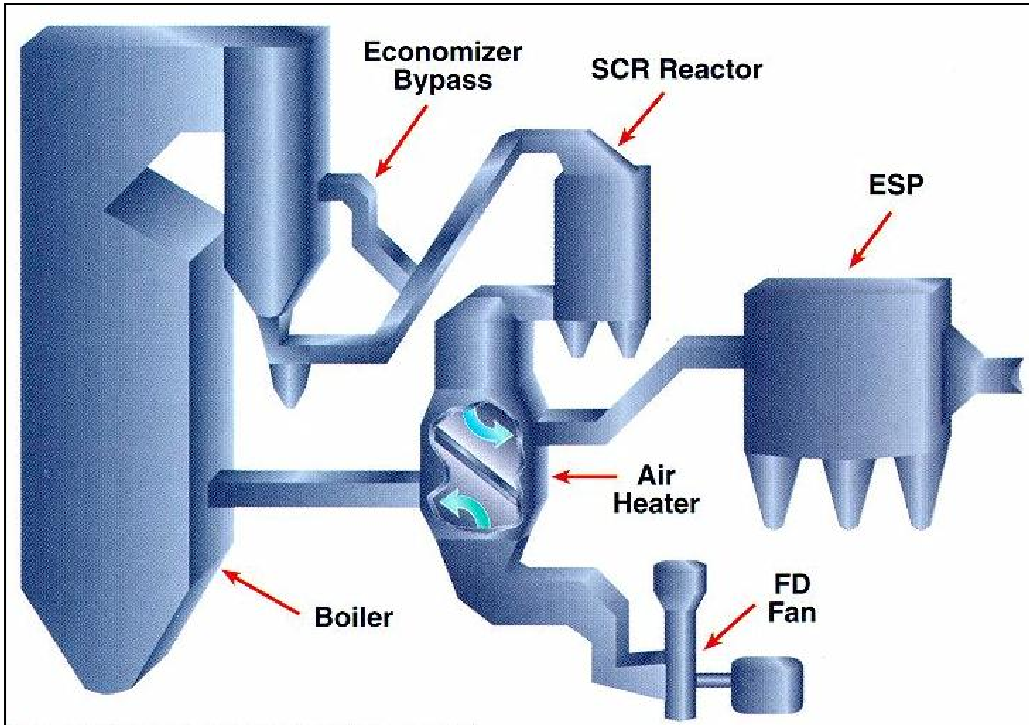
$$SO_2 + 1/2\ O_2 \longrightarrow SO_3$$

$$2NH_3 + SO_3 + H_2O \longrightarrow (NH_4)_2SO_4$$

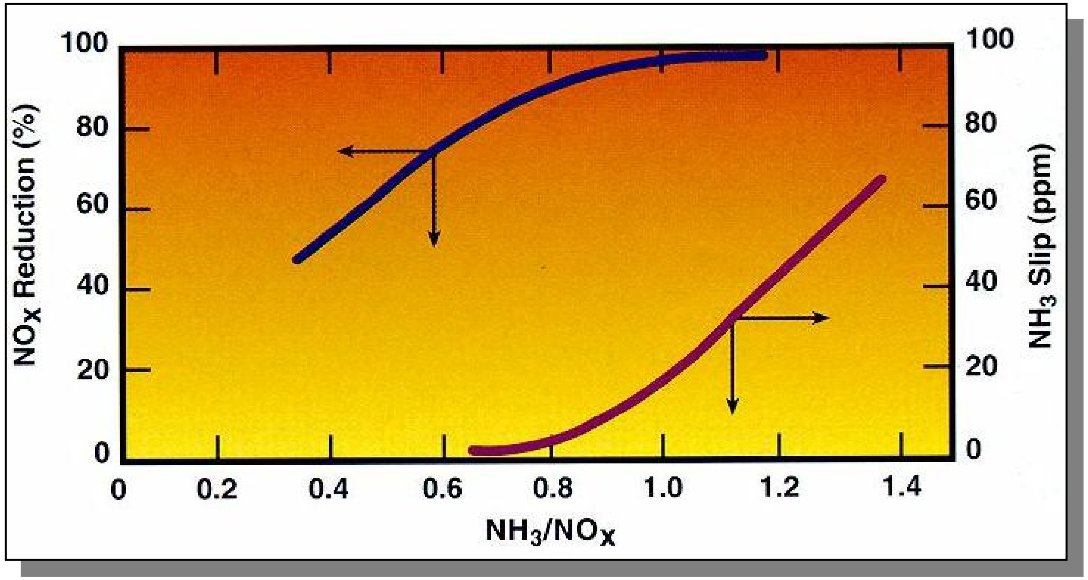
$$NH_3 + SO_3 + H_2O \longrightarrow NH_4HSO_4$$



Vertical-flow fixed-bed type reactor chamber

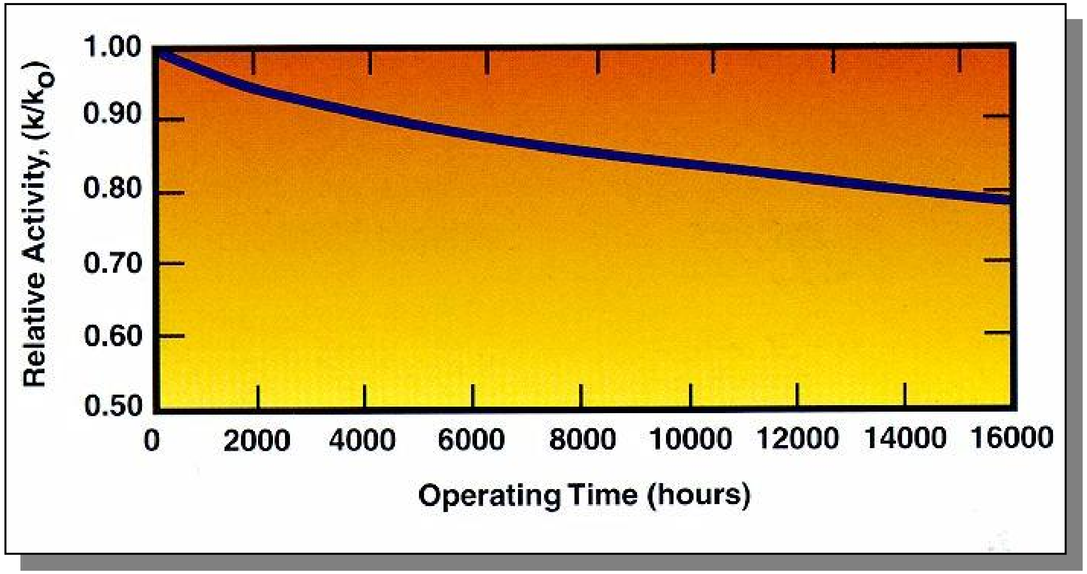


Selective catalytic reduction (SCR) of NOx /2



Efficiency and ammonia slip (↑)

and catalyst activity (→)

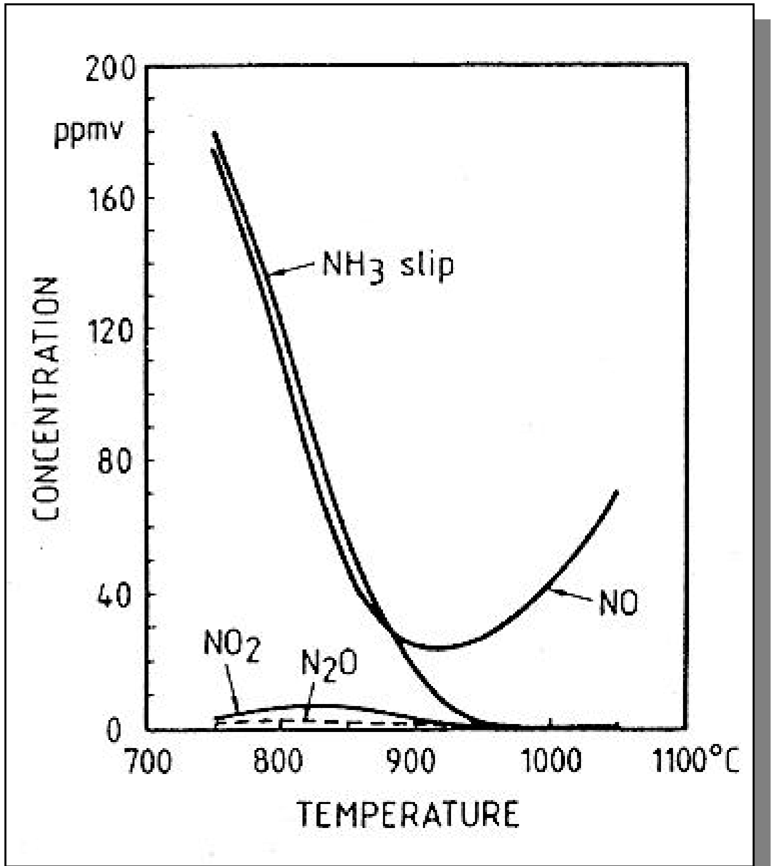


A damaged SCR unit: damaged catalyst

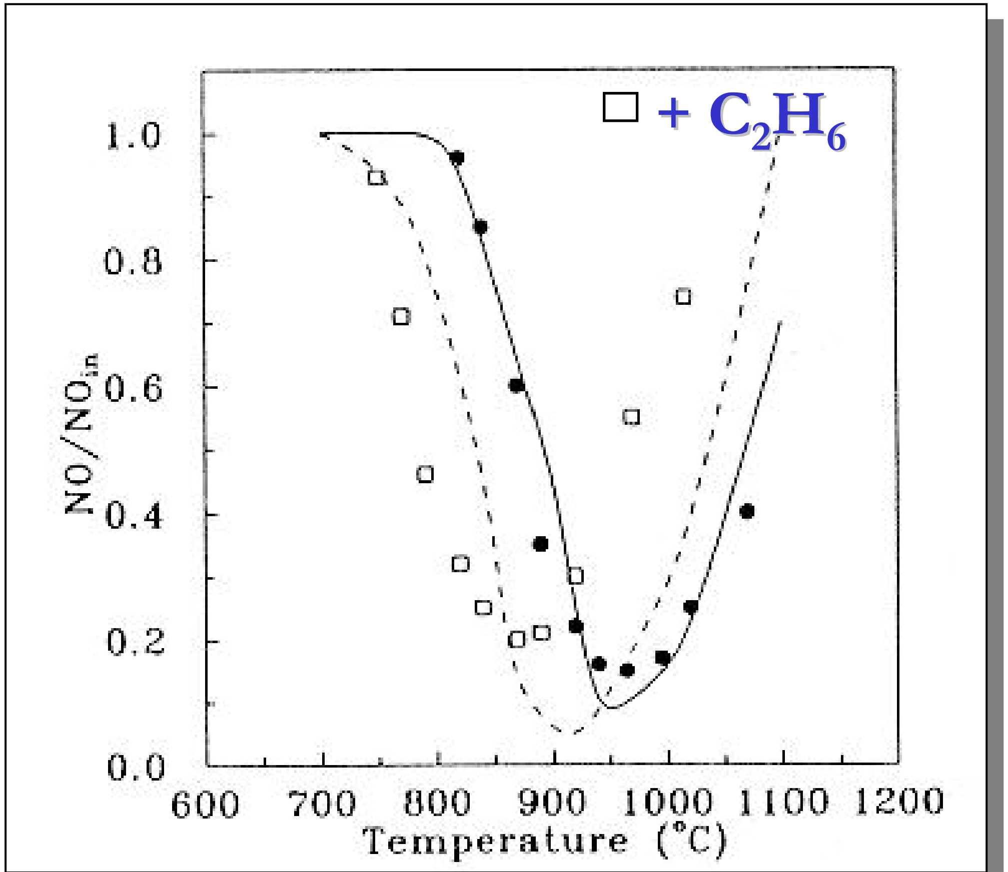

Bild 2. Zerstrahlte Katalysatorsteine und leere Hülse.


Bild 3. Zerbrochener Katalysatorstein.

Selective Non-catalytic NOx reduction (SNCR)



Effect of temperature



Effect of C_2H_6 addition

NOx removal from flue gases : other methods

- Copper oxide process for simultaneous DeSOx / DeNOx
- dry absorption on activated carbon at ~220°C :

$$NOx + SO_2 \xrightarrow{+ \text{carbon} + H2O + O2} N_2 + H_2SO_4$$

- Wet scrubbing with water after oxidation of NO

Gas phase: $NO + O_2 \rightarrow NO_2, N_2O_4, N_2O_5, HNO_2$

Liquid phase: $NO_2, N_2O_4, N_2O_5, HNO_2 \xrightarrow{+ H2O} HNO_3$

- Wet scrubbing with "chemical enhancement" (NaOH, KMnO4)
- Electron beam irradiation
- Phosphorous : catalyses oxidation of NO to NO_2