

REINHOLD ENVIRONMENTAL Ltd.



2011 NO_x-Combustion Round Table & Expo Presentation

February 7-8, 2011, in Birmingham, AL / Hosted by Southern Company

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SCR DeNOx catalyst considerations when using biomass in power generation

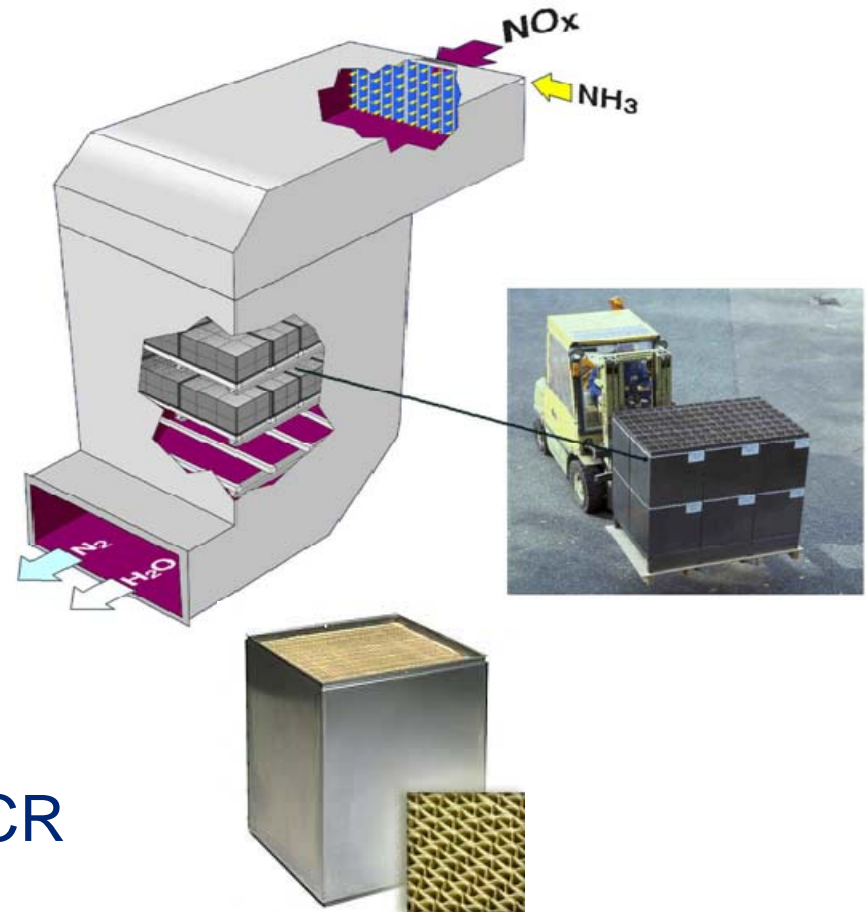
RESEARCH | TECHNOLOGY | CATALYSTS

Hans Jensen-Holm, Haldor Topsoe, Denmark

Reinhold 2011 NOx-Combustion Round Table

Contents

- Biomass sources
- Catalyst deactivation
 - What deactivates the catalyst?
- Biomass in power production
 - High-dust co-combustion
 - High-dust 100% biomass
 - Low-dust 100 % biomass
- Low-dust versus high-dust SCR



Why biomass?

Drivers for biomass in power production

- Political and social concerns about global warming (CO₂ neutral)
- Wildly available, “renewable”
- Economical (incited)

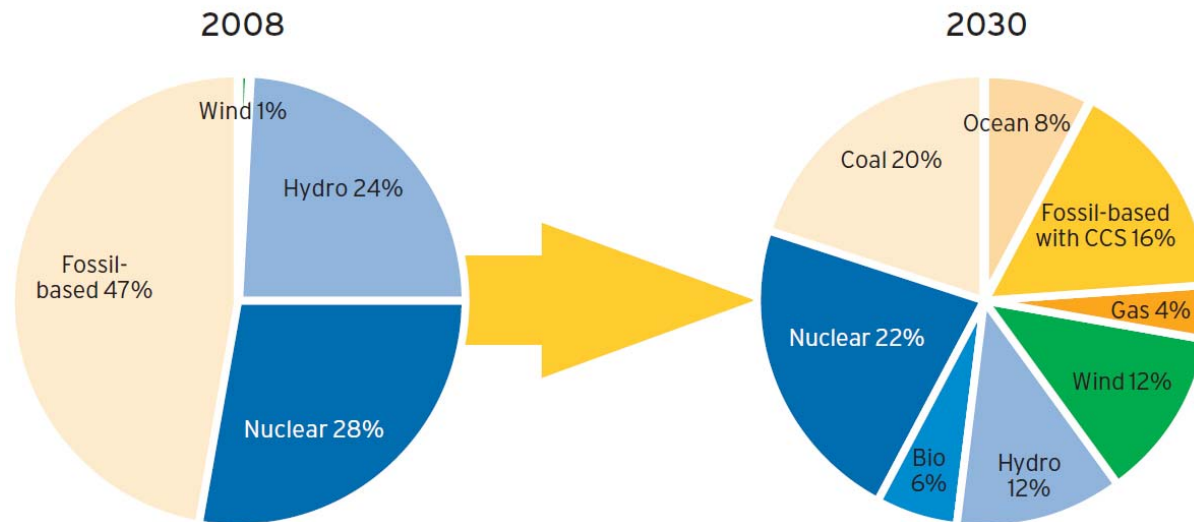


CSR – Corporate Social Responsibility

- DONG Energy, 2009 (Anders Eldrup, CEO):

“Within a generation we will turn our power- and heat production upside down from today being based on 85% fossil energy and 15% renewable energy to be based on only 15% fossil energy and 85% renewable energy

- Vattenfall:

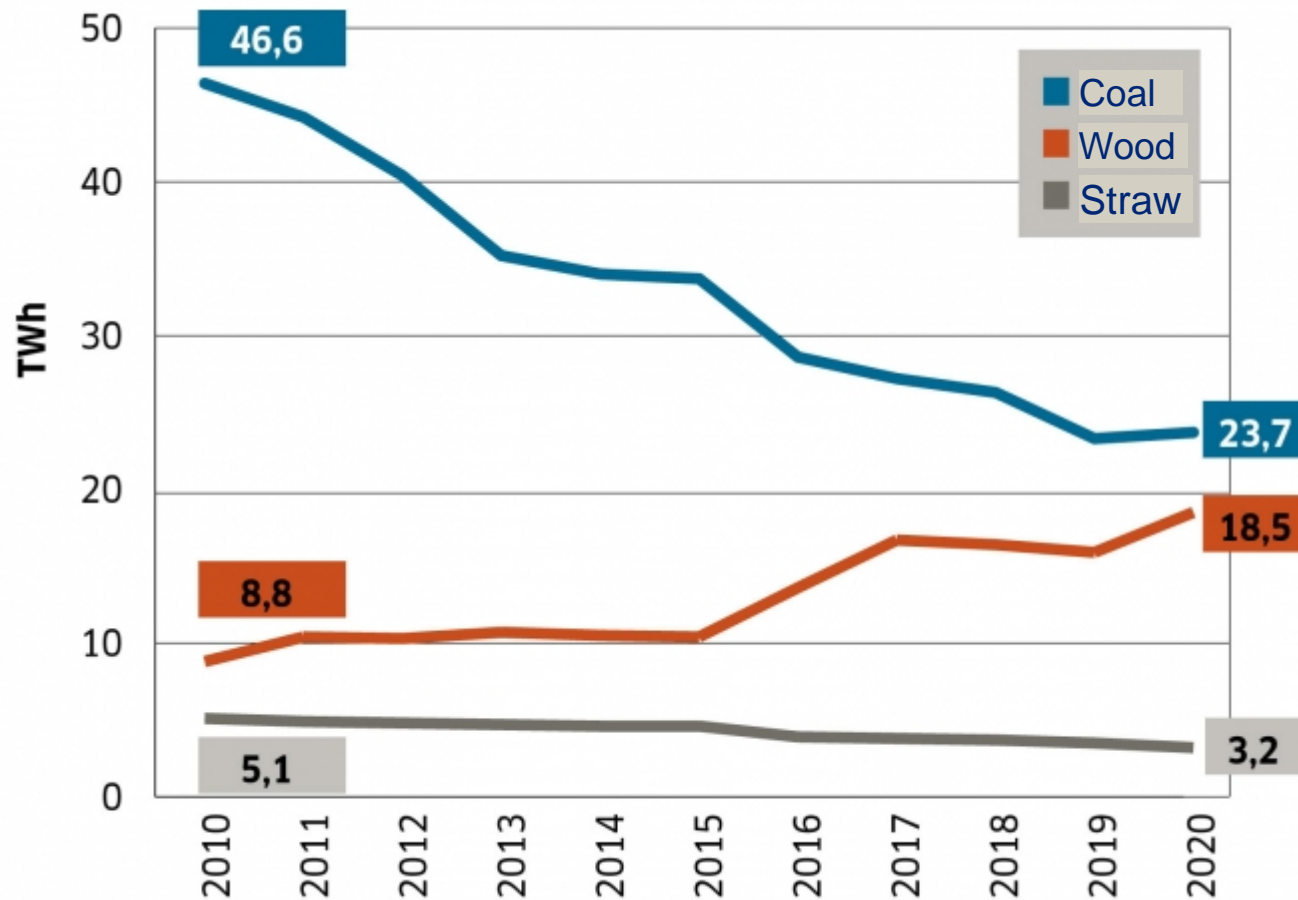


- E.ON:

“E.ON’s goal is to halve the carbon intensity by 2030 from 1990 levels”

Biomass has come to stay

Projection of fuels in Danish energy supply



Source: Force Technology, Denmark

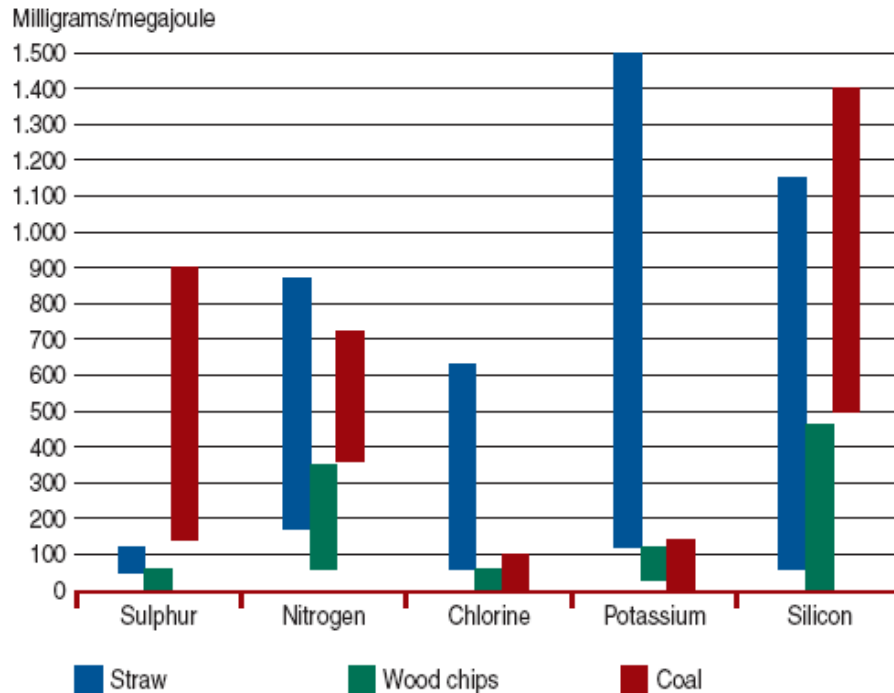
Biomass sources

Possible biomass sources comprise e.g.:

- Wastes and residues:
 - Wood and bark: forest or tree trimmings, sawdust, demolition wood, crates, sleepers
 - Agricultural residues: straw, olive residue, coffee grounds, almond shells, rice hulls, bagasse, coconut chips
 - Animal wastes: Poultry litter, meat bone meal
 - MSW, sewage sludge, paper waste
- Peat
- Agricultural energy crops (quick growing):
 - Switchgrass
 - Miscanthus
 - Poplar and willow
 - Bamboo
 - Etc.



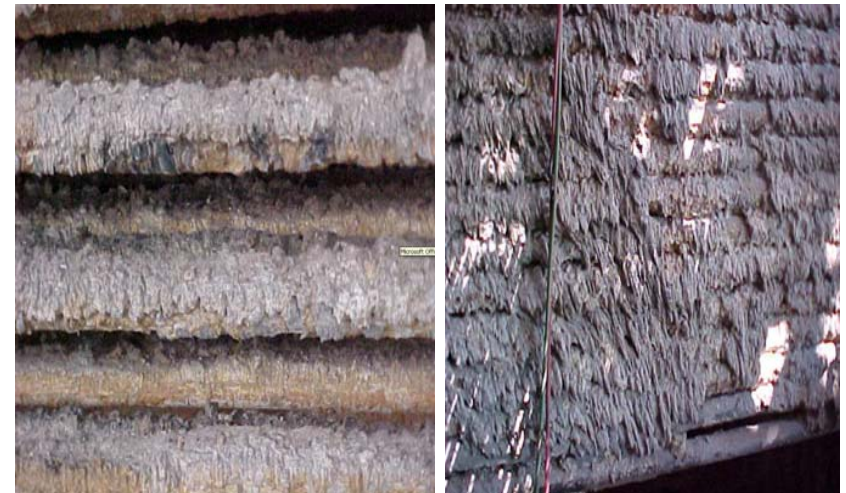
Biomass as fuel for power production



Fuel	Water content	Calorific value
Coal	10%	25MJ/kg
Wood pellets	8%	17.5MJ/kg
Straw	14%	15MJ/kg
Wood chips	45%	9.5MJ/kg

Technical challenges:

- low energy density – large volumes
- difficult handling properties
- working environment – dust and fungal spores
- potassium and chlorine
 - slagging, fouling and corrosion
 - flue gas cleaning
 - utilization of residues

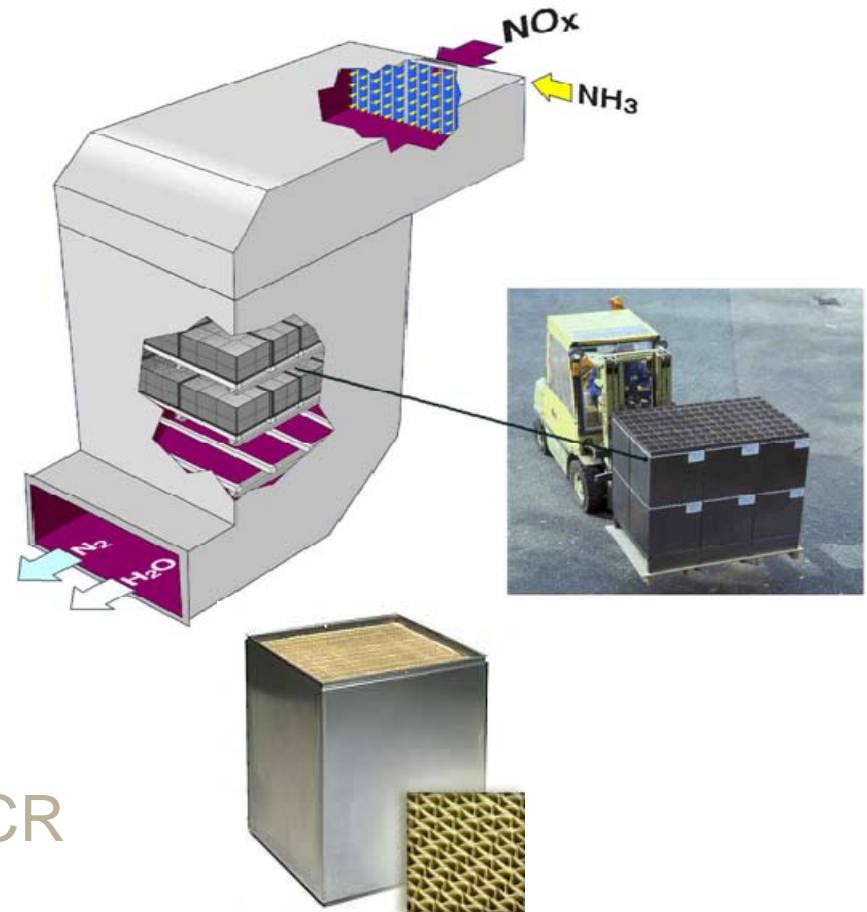


Biomass fuel - ash analysis, examples

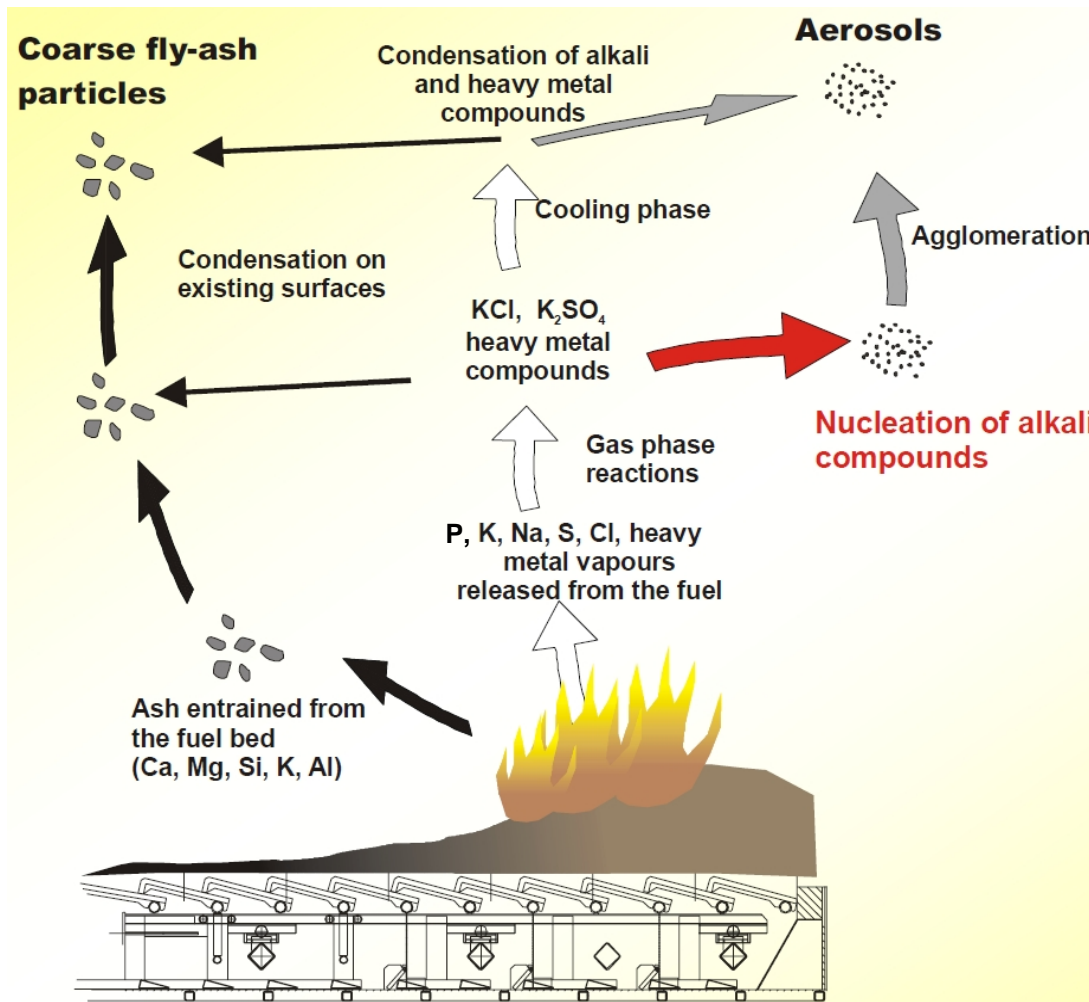
	Sulfur, wt%	Ash, % dry	K ₂ O	Na ₂ O	P ₂ O ₅	CaO
Pine chips	0.02	0.3	15.3	2.0		
Wood pellets	0.03	0.5	9.4	1.3	2.9	29
Willow chips	0.04	1.6	15.1	1.0	9.4	
Peat, Finnish	0.19	3.8	1.1	0.1	2.7	9.8
Miscanthus low K	0.1	1.5	22.3	1.2	6.2	6.3
high K	0.1	1.1	5.3	1.3	6.5	12.7
Wheat straw, Danish	0.1	4.7	16.9	0.4	2.3	7.3
Corn stalks			10.3	0.3	0.7	0.5
Olive residue	0.06	10.8	17.3	4.5	3.4	13

Contents

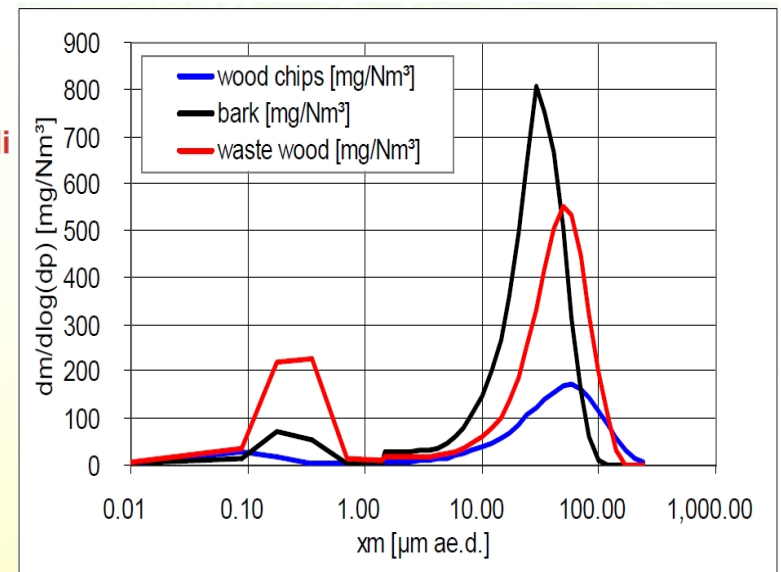
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Biomass combustion products

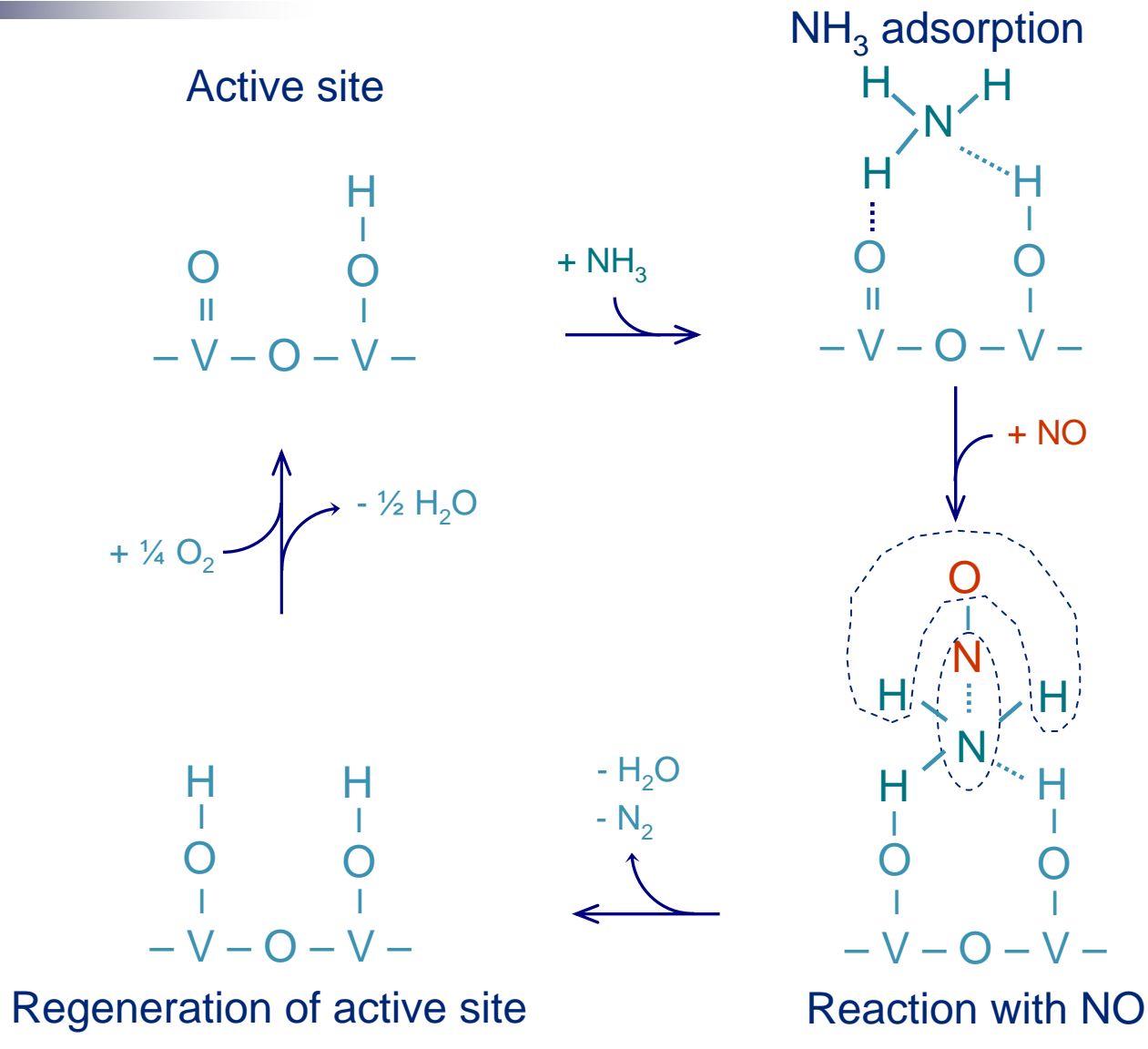


Typical particle size distributions of aerosols and fly ashes formed from burning of woody fuels

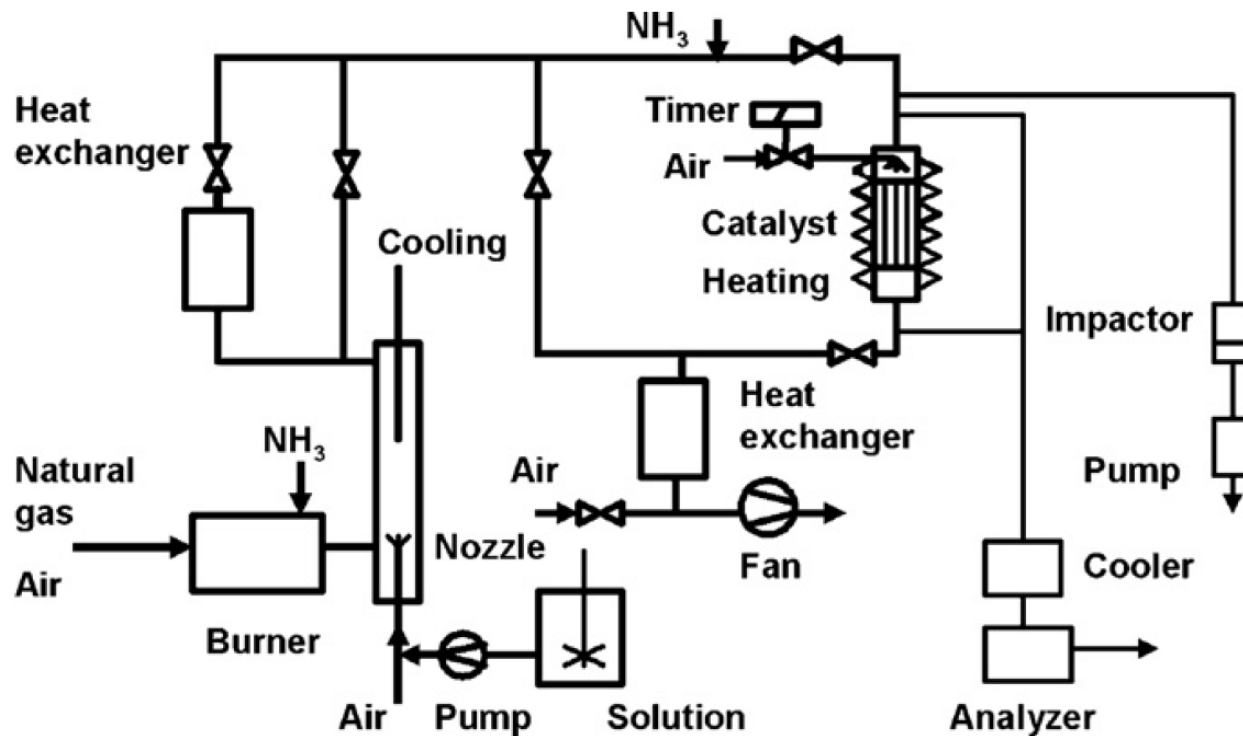


From: Ingwald Obernberger, "Aerosols and fly ashes from fixed-bed biomass combustion"
Annual ACERC Conference 2003

SCR DeNOx reaction mechanism

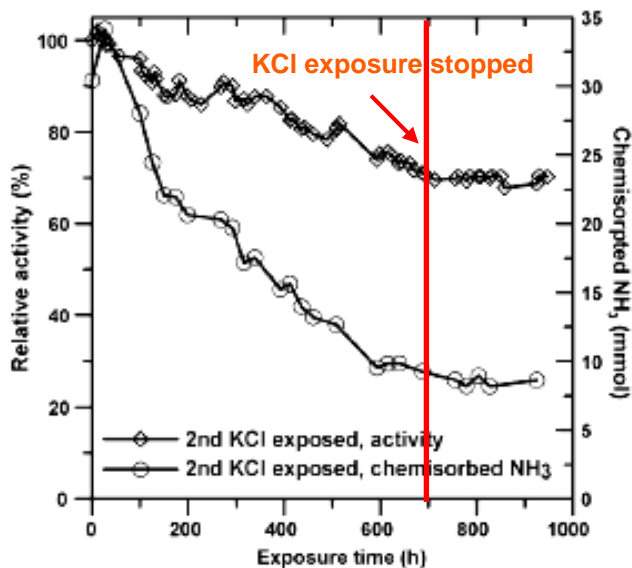


Test of catalyst exposure to potassium salts



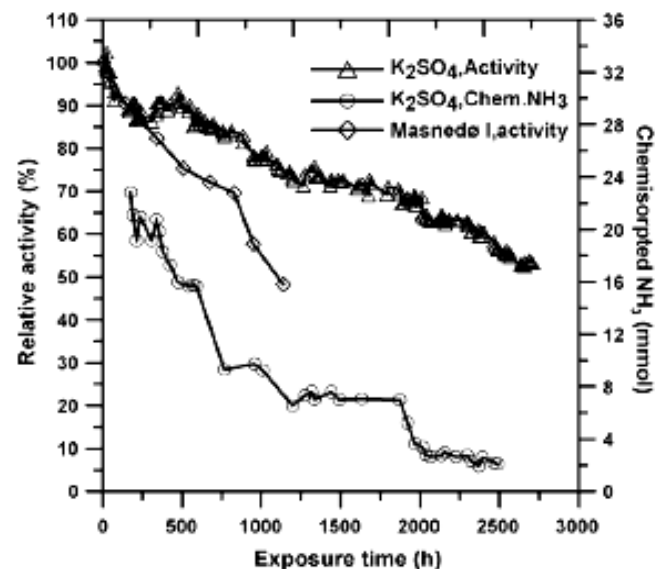
Bench-scale experiments with furnace injection of potassium-salt solutions

KCl aerosols



Deactivation 50%/1,000 hrs

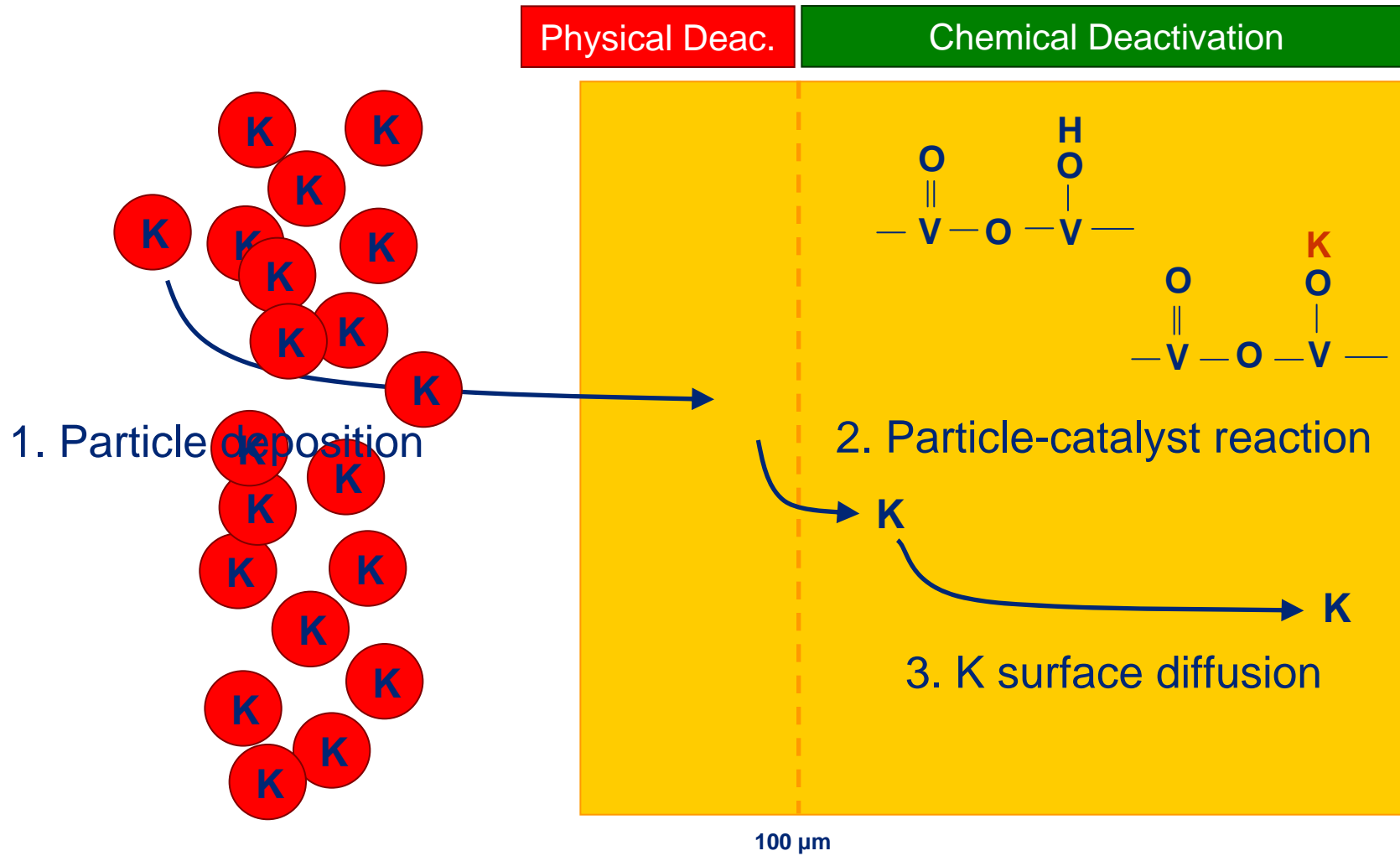
K₂SO₄ aerosols



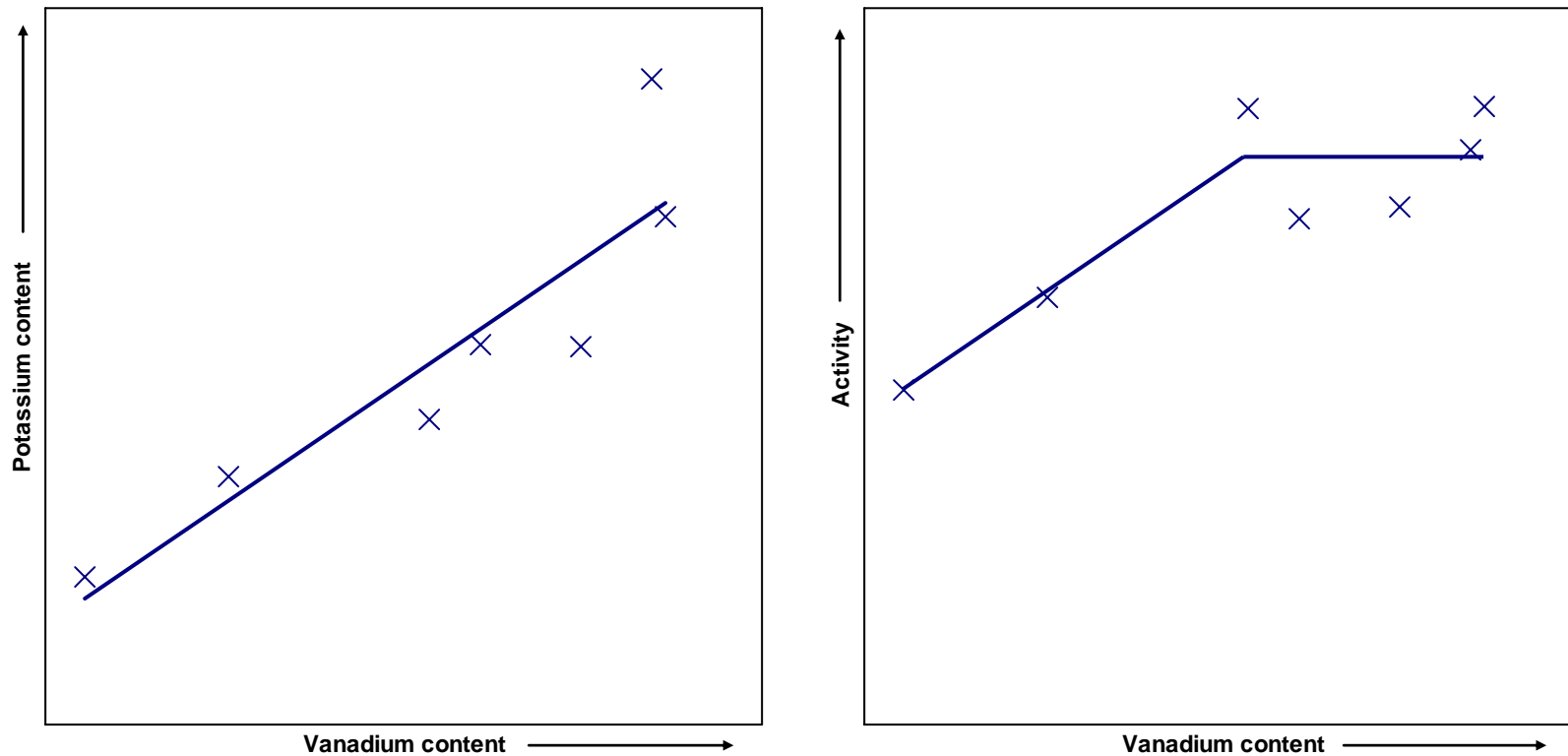
Deactivation 30%/1,000 hrs

- Continuous flow of aerosol through the catalyst is required for deactivation
- Impregnation experiments show the same effect of sulfate and chloride
- Difference between sulfate and chloride deactivation rates indicates an effect of surface diffusion mobility or aerosol deposition rate

Alkali-metal deactivation mechanism



Alkali deactivation – Influence of vanadium



Catalyst coupons exposed to a KCl-aerosol containing flue gas for 850 hours at 662 °F

Alkali-metal deactivation

Relative activity compared to fresh catalyst, %	As received	After 1-hour exposure to 850°F
Measured at 485°F	57	29
Measured at 665°F	49	19

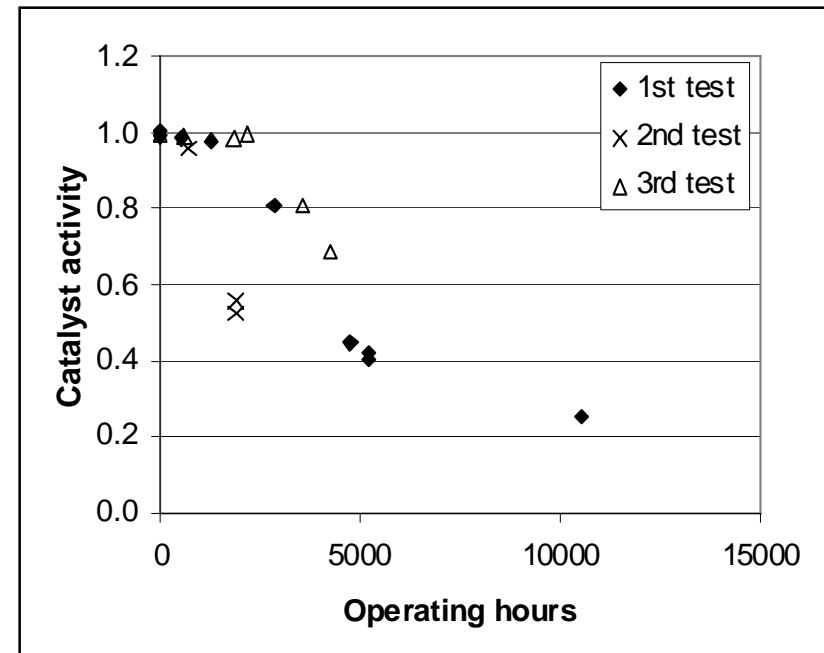
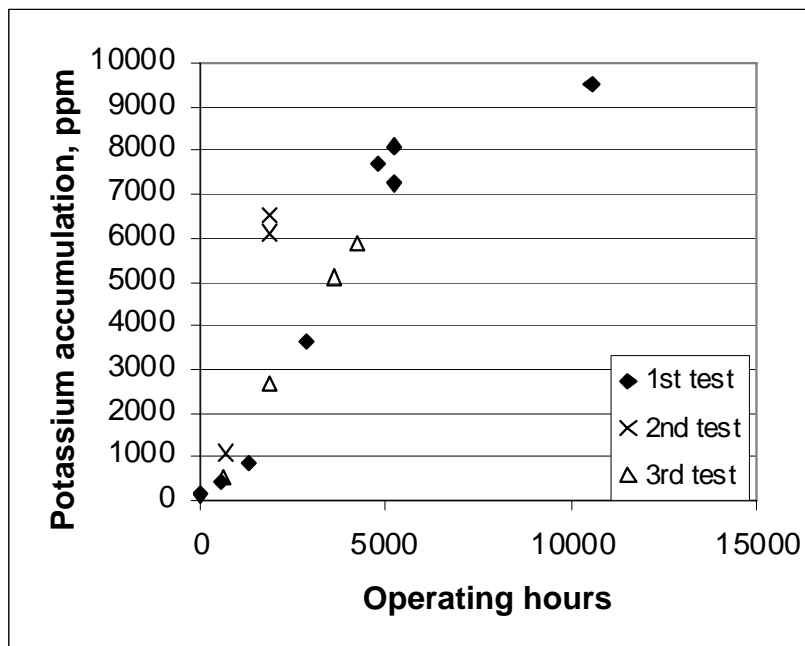
- Deactivation appears higher at higher temperature
- The reaction rate is determined by:
 - At low temperature: number of redox-sites ($V=O$)
 - At high temperature: number of NH_3 -adsorbing sites ($V^{+5}-OH$)
- Activity drops by more than 50% by high-temperature exposure
 - Redistribution of potassium
 - Release of potassium from surface deposits

Alkali-metal deactivation

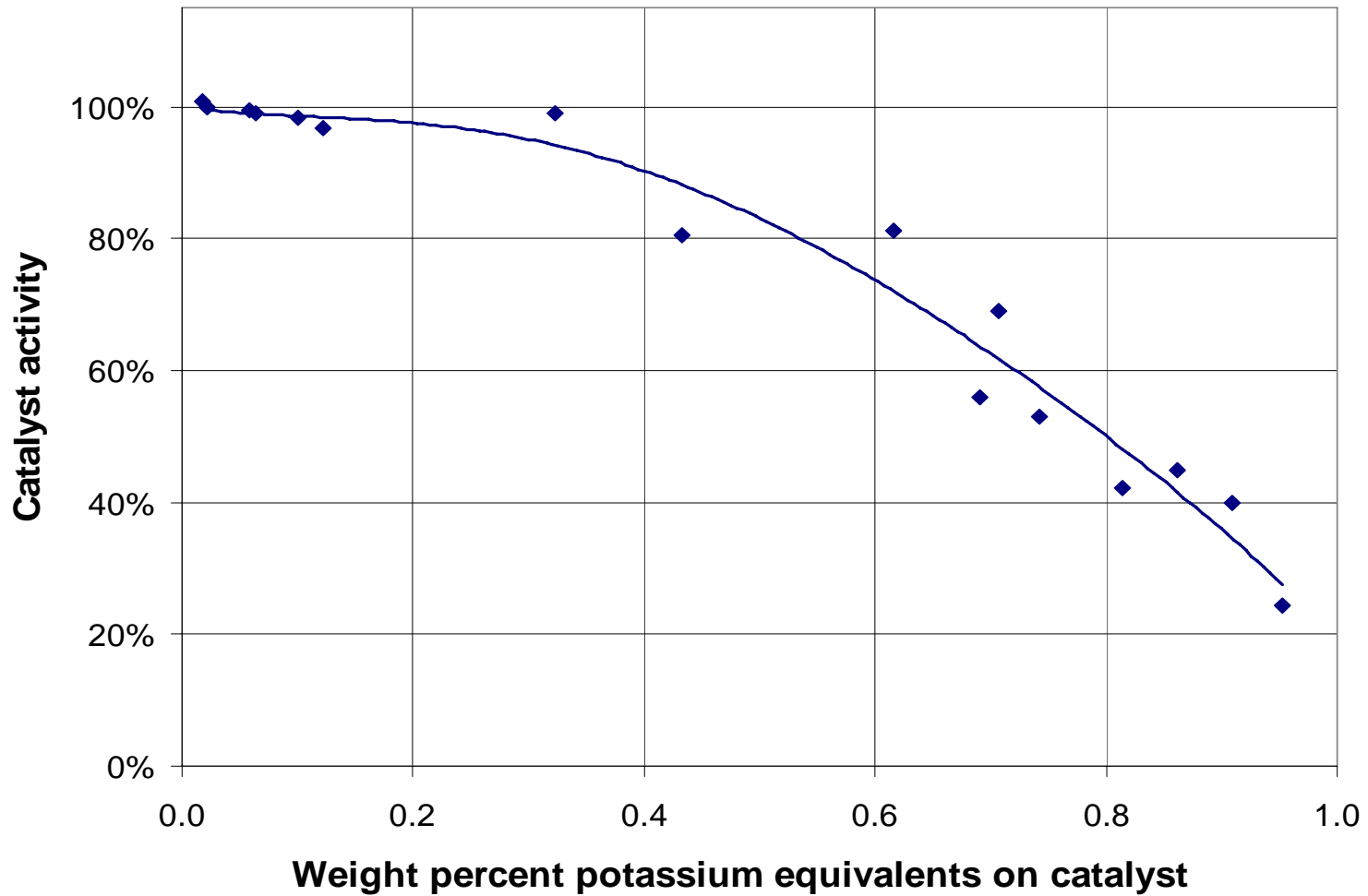
CFB boiler, 100% wood chips,

Catalyst sample plates installation on Nässjö CHP, Sweden

Temperature: 392 °C / 738 °F



Alkali-metal deactivation



Deactivation by phosphorous

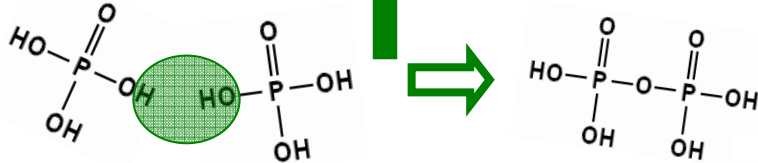
Organically bound phosphorous

Combustion 1400°C / 2550°F

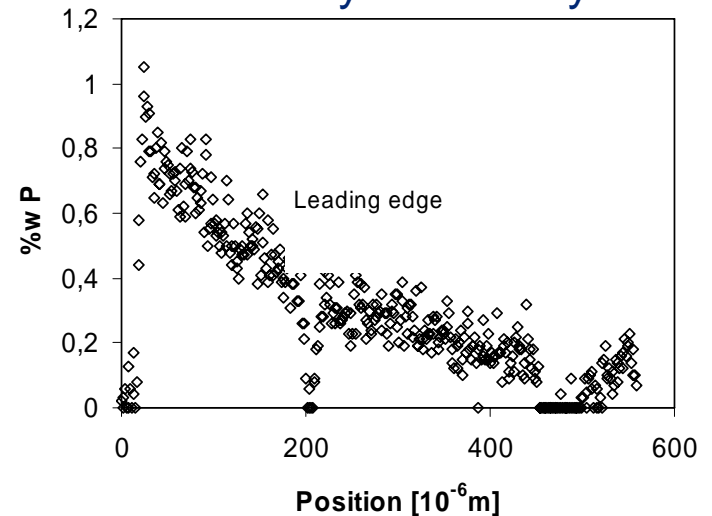
Gas-phase phosphorous

Cooling

Sub micron P-containing particles

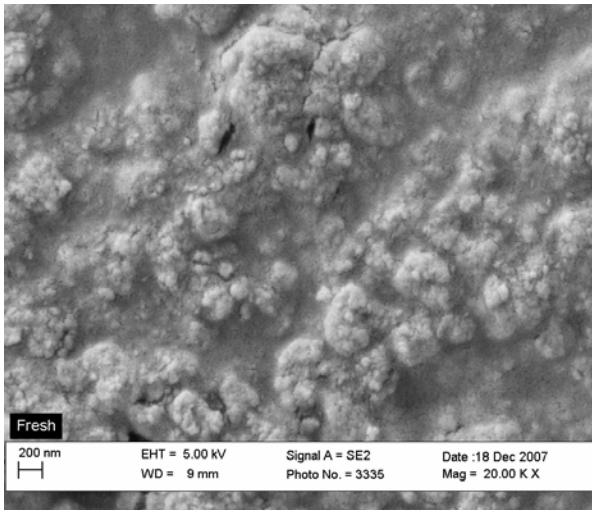


P-mobility into catalyst



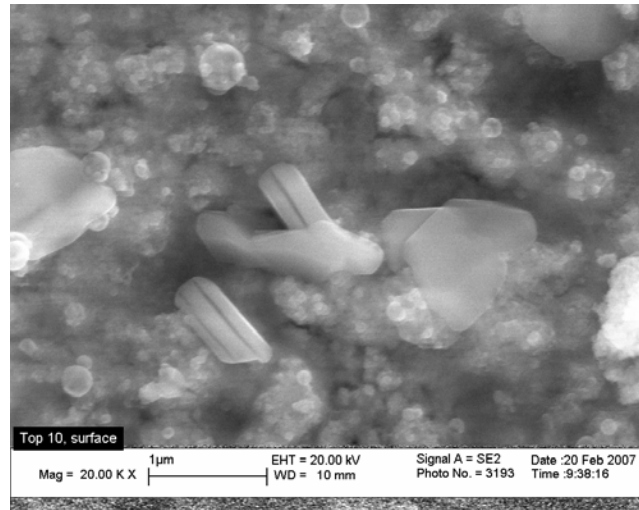
Result: Pore blocking, surface masking, reaction with V=O sites

Catalyst surface fouling by polyphosphate



Fresh catalyst surface

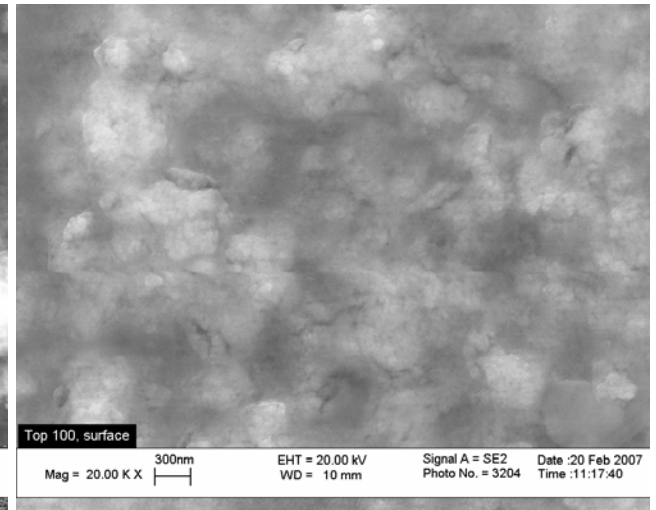
Pore volume (ml/g): 0.74
 Pore area (m²/g): 55



Exposed to 10 ppm H₃PO₄

The porous structure of titania is still distinguishable. Some needle-shaped crystals are present. Analysis by EDX showed enrichment in P

Pore volume (ml/g): 0.55
 Pore area (m²/g): 50



Exposed to 1000 ppm H₃PO₄

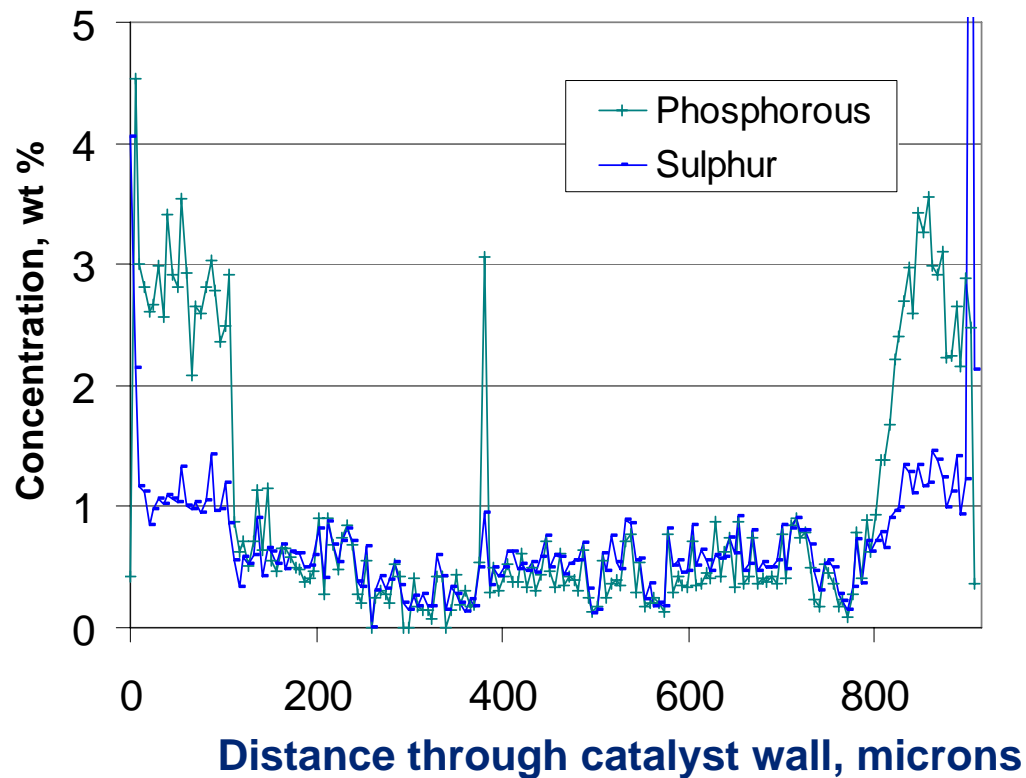
The surface is uniformly covered by a glassy layer

Pore volume: 0.08
 Pore area (m²/g): 21

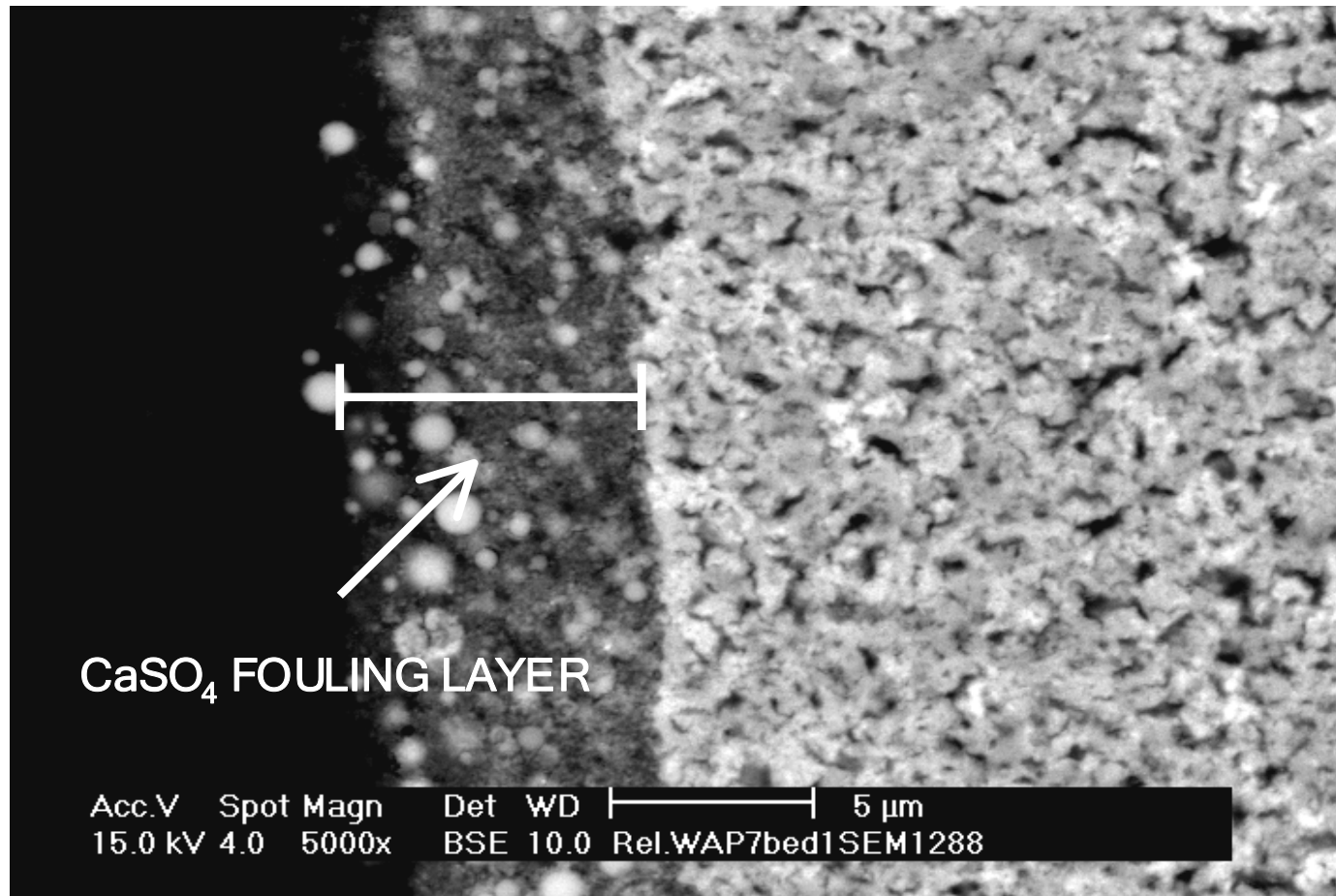
Deactivation by phosphorous

Catalyst wall cross section

Sub-surface phosphorous layer in the outer 50-100 microns of the surface of a catalyst exposed to flue gas from phosphorous-containing fuel (PRB coal)



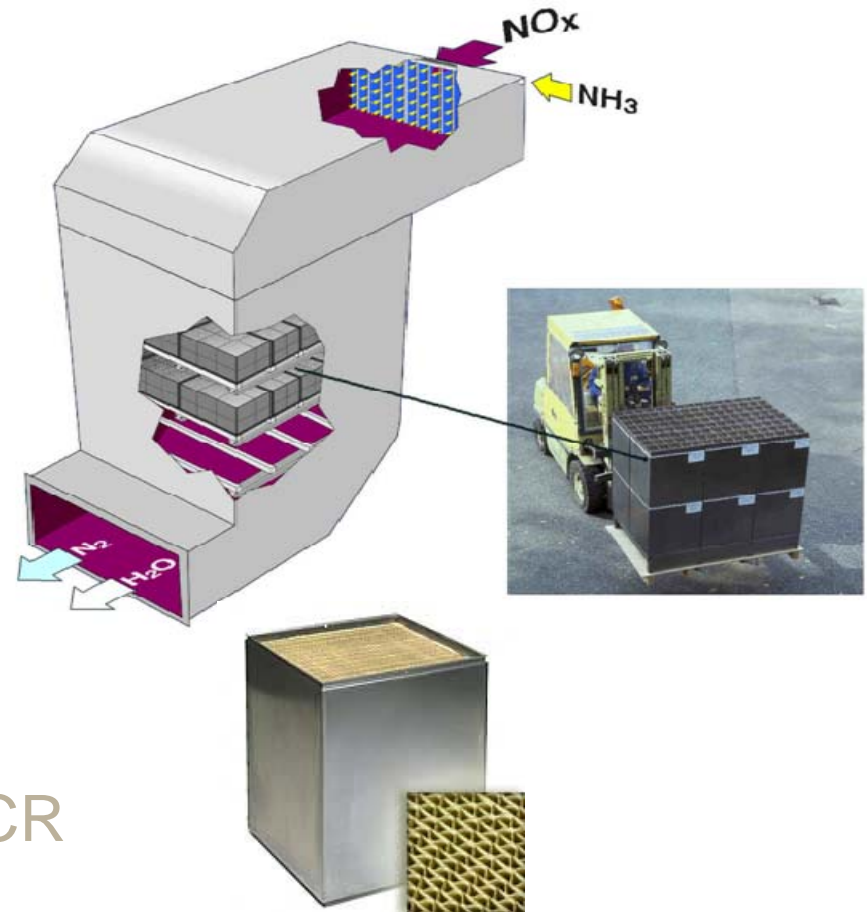
Surface deposition of calcium sulfate



Result: Impedes gas diffusion and reaction

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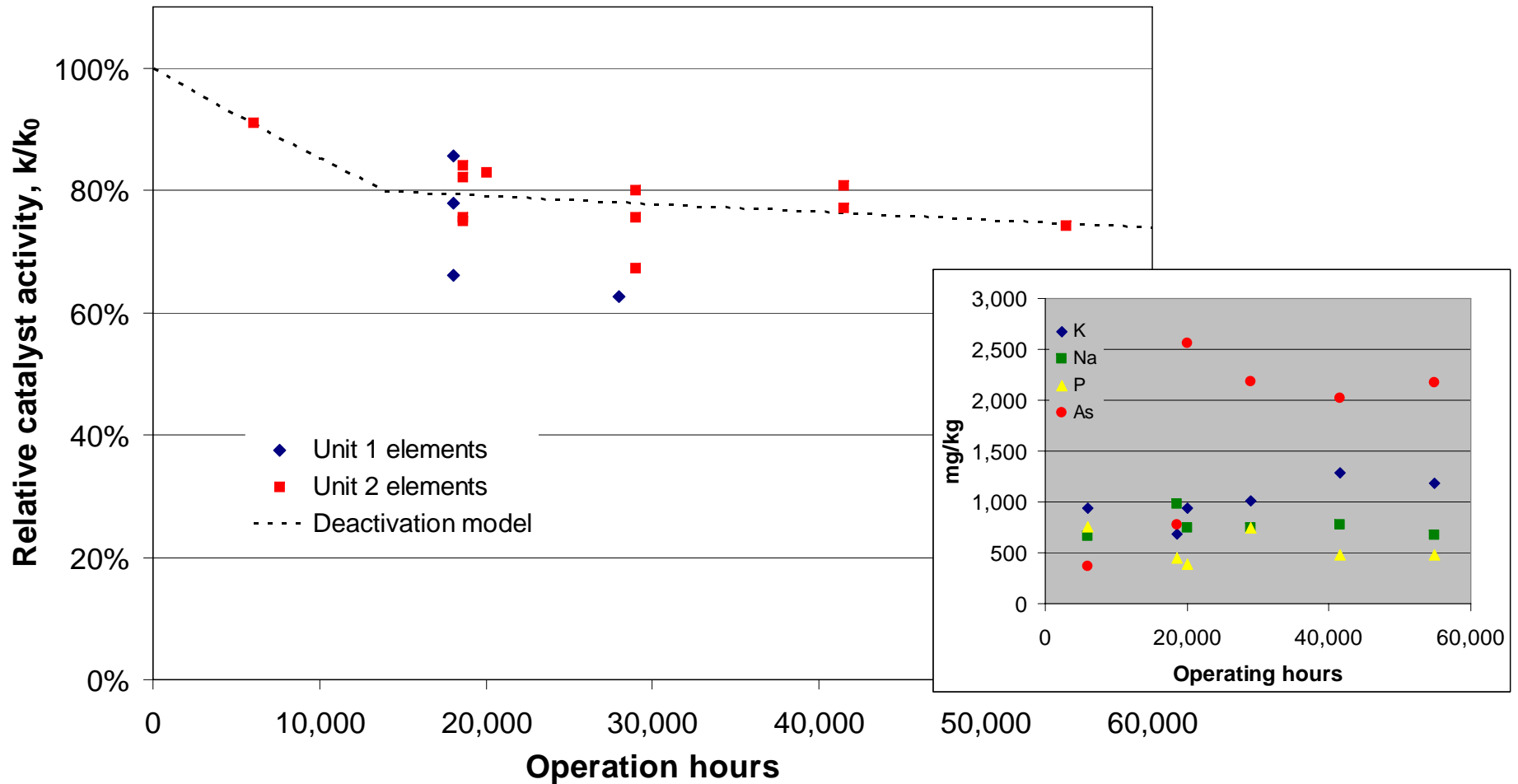


EON, Langerlo Power Station, Belgium

- Capacity: 2 x 250 MW_e
- Fuel (by mass):
 - Biomass co-firing since 2002
 - 60-65% South African coal
 - 25-30% USA CONSOL
 - 3% olive residue
 - 4% dried municipal sewage sludge
 - 7% wood dust
- Fuel blend ash
 - Phosphorous, potassium, arsenic



Catalyst deactivation at EON's Langerlo Power Station, Belgium



DONG Energy, Studstrup Power Station

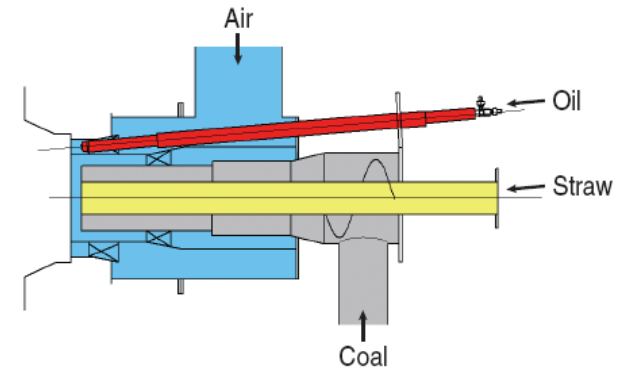
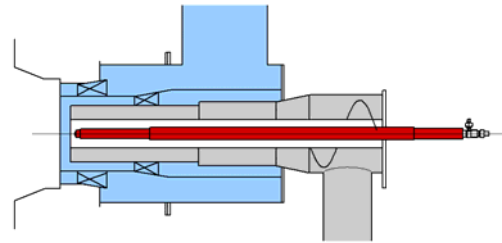
- 2 x 350 MWe
- 10% straw on energy basis has been co-fired since 2002 and 2005 in the two units
- SCR installed 2007



Co-firing of straw at Studstrup

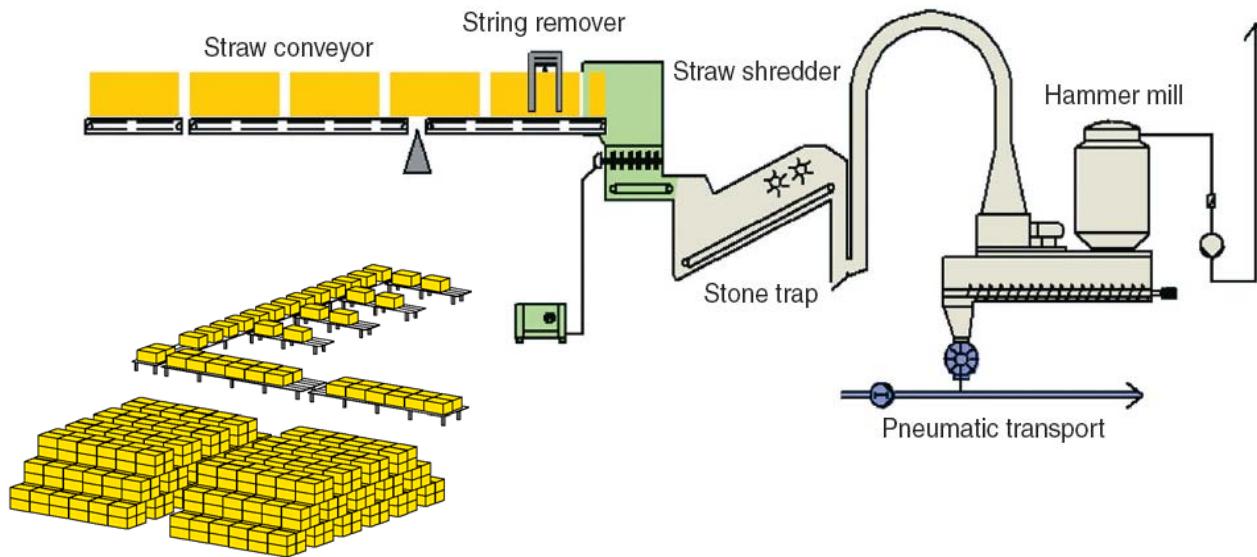
Focus areas:

- combustion
- straw handling
- superheater corrosion
- fly ash utilization
- SCR catalyst deactivation



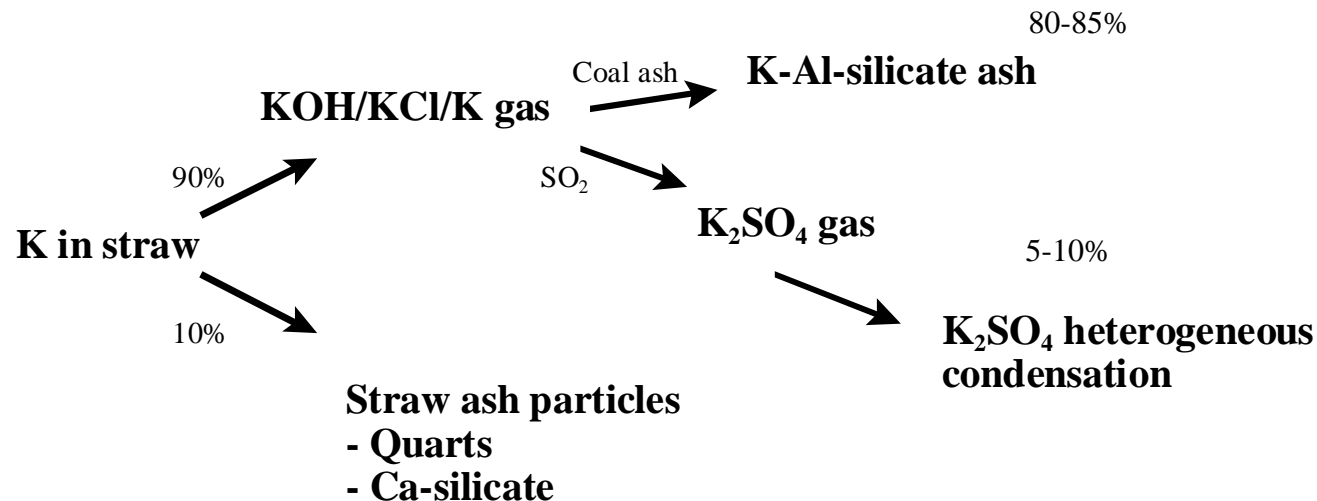
Straw-handling plant

Combined coal/straw burner



Ash chemistry by co-firing of straw

- No increase of LOI/unburned carbon in fly ash by 10% straw co-firing
- Content of K_2O , CaO , P_2O_5 , SO_3 and Cl may increase by co-firing, dependent on coal and straw composition, combustion conditions and straw share
- Low capture of Cl in ash
- No increase in formation of submicron particles
- 5-10% of potassium from straw is found as water soluble potassium in fly ash (potassium sulfate)
- >80% potassium from straw is captured as potassium-alumino-silicates by reaction with coal ash

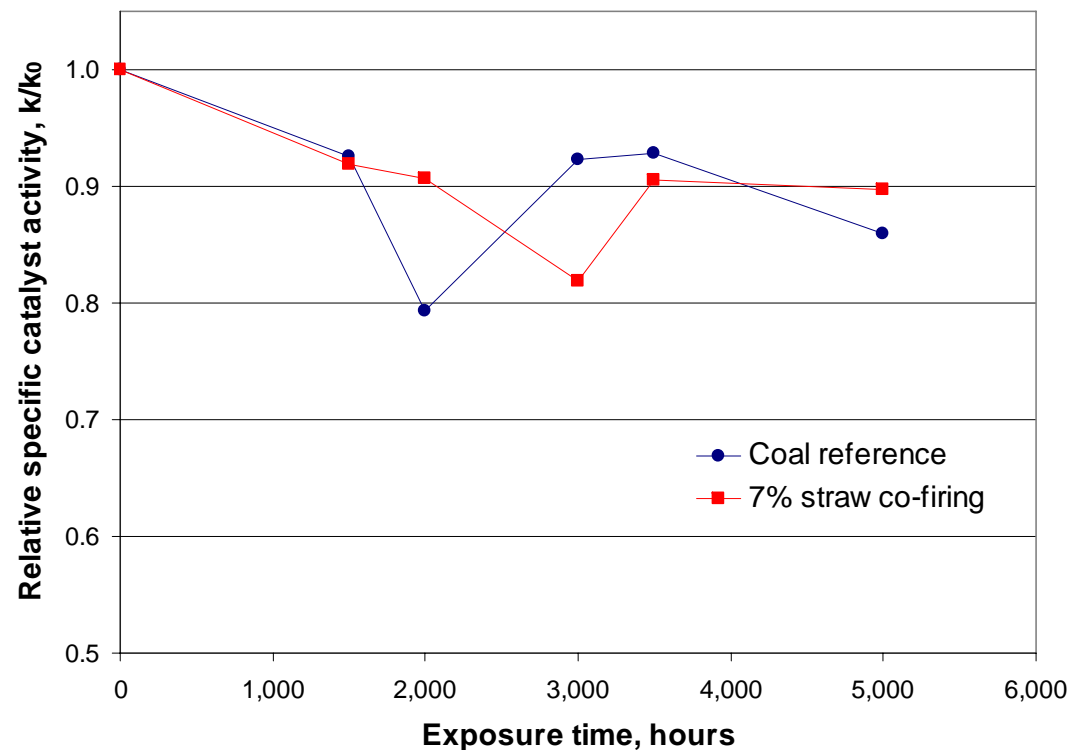


Fly ash utilisation and catalyst deactivation

Fly ash utilization:

- For cement (low alkali coal must be applied)
- For concrete (max. 20 weight% straw equivalent to 13% on energy basis)

No poisoning of SCR catalysts by potassium observed during 5,000 hours test in pilot:

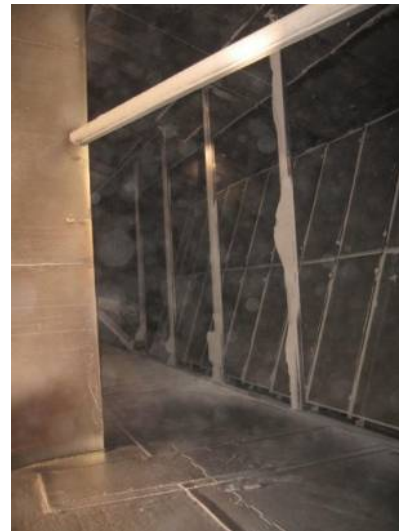
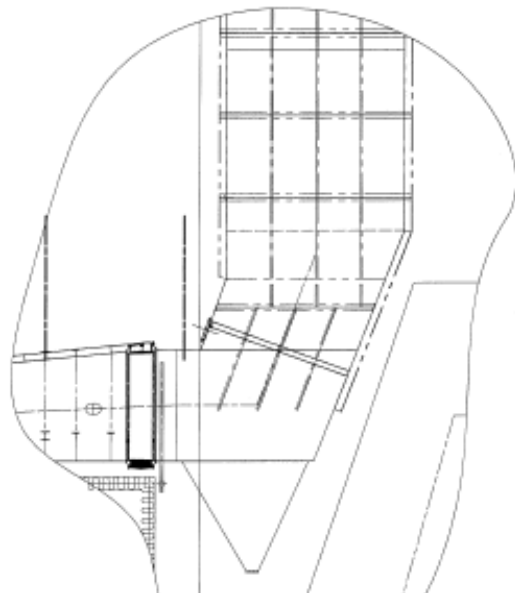
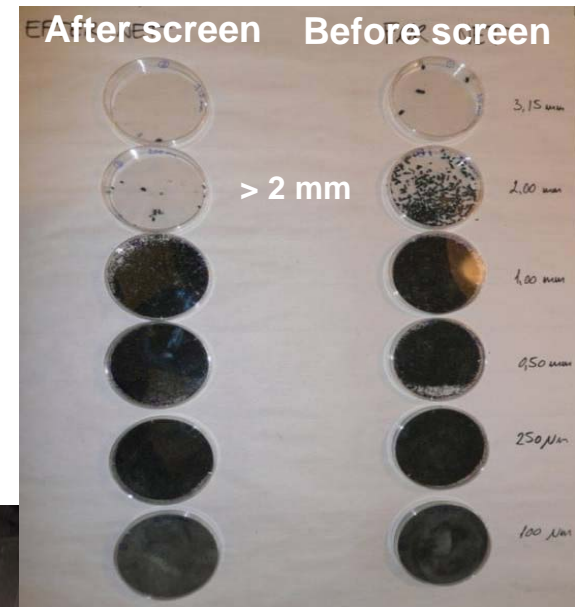


Full scale SCR

- Commissioning of full scale SCR plants at Studstrup power plant in 2007
- Severe plugging of catalyst after a few weeks of operation
- Plugging caused by straw char particles due to incomplete burn-out



Ash screens installed for protection of catalyst



Ref: DONG Energy, Expperts 2008 Brussels

Washing of catalyst



- Washing of catalysts removed most of the plugging
- Activity of element from Unit 4 after 14,000 hours: 89% (10% straw on energy basis)