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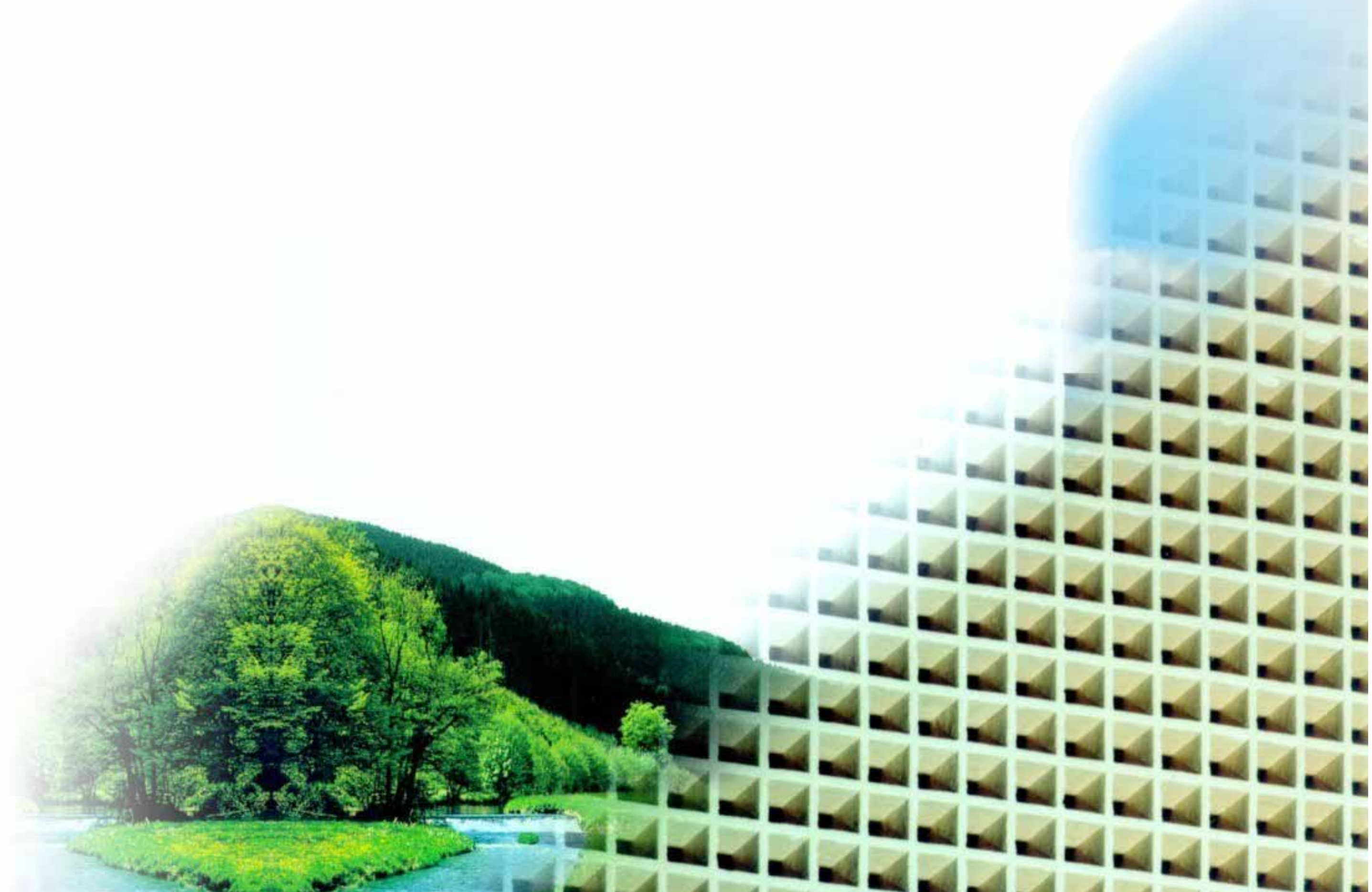

2007 NOx/PGUC Conference

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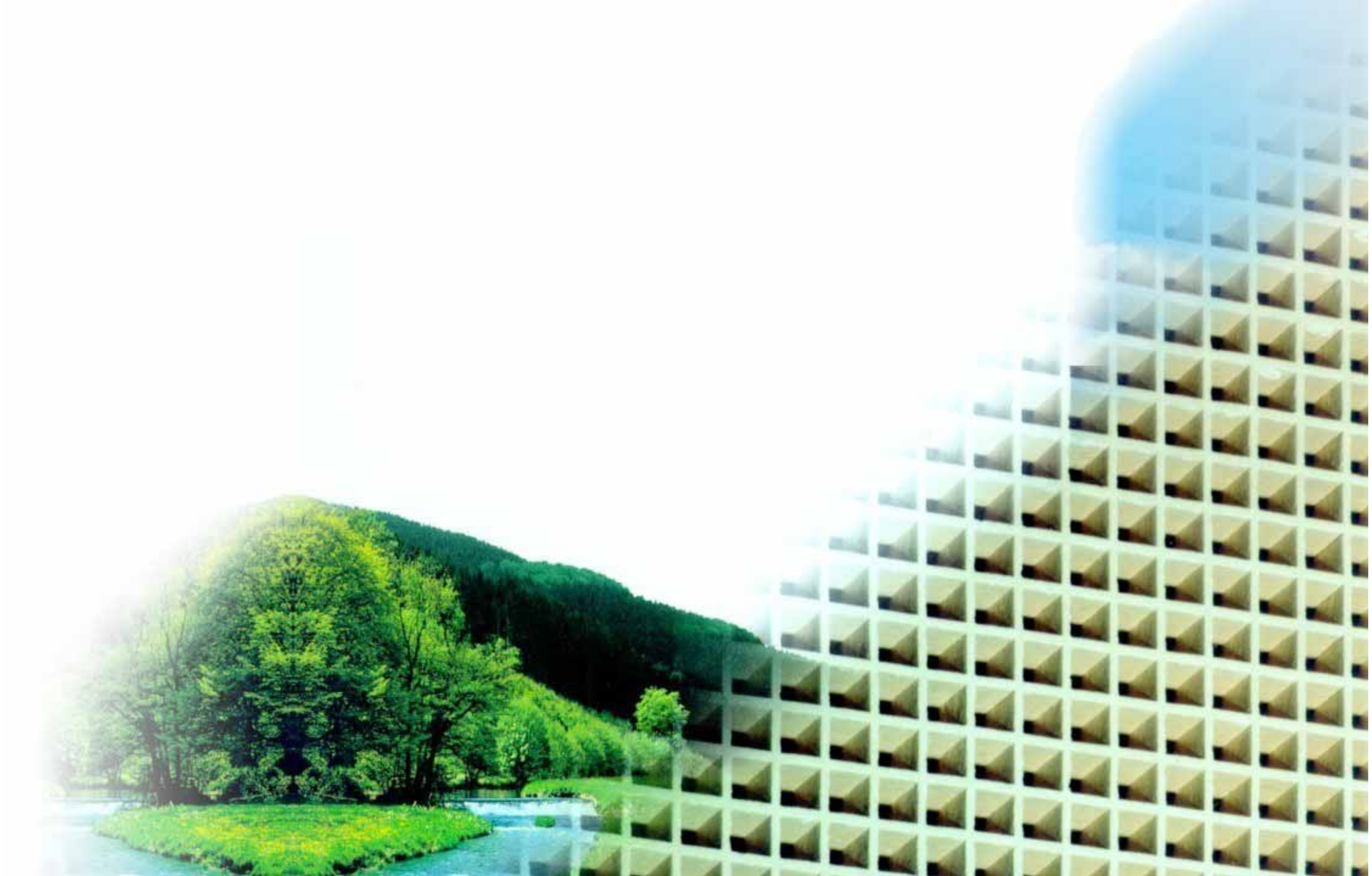

Workshop VI: SCR Catalyst Poisoning

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SCR catalyst poisoning: outline

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- SCR catalyst – Focus on Coal fired applications (No Cat crackers, incinerators, nitric acid plants, …)
- Fuel types and constituents
- Deactivation mechanisms
- Poisoning
    - mechanisms
    - mitigation
- Operational considerations
- Conclusions
- Questions

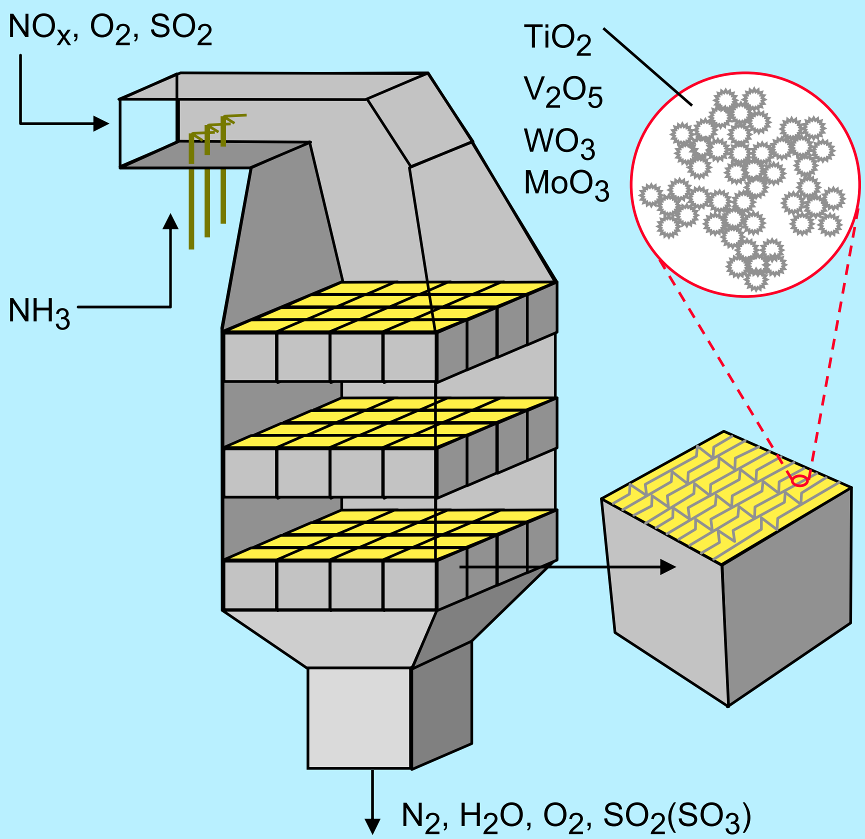
Selective Catalytic Reduction - Principles
Main Reactions

- Ammonia injection in flue gas.
- The flue gas + ammonia passes through a catalyst bed in a reactor.
- On the catalyst surface ammonia reacts with nitrogen oxides to form molecular nitrogen and water vapor.
- First order reaction: $r_{NO} \sim k\ C_{NO}$
- Mass transport (diffusion) limited

$$4\ NO + 4\ NH_3 + O_2 \xrightarrow{\text{Cat.}} 4\ N_2 + 6\ H_2O$$

$$6\ NO_2 + 8\ NH_3 \xrightarrow{\text{Cat.}} 7\ N_2 + 12\ H_2O$$

Selective Catalytic Reduction - Principles



Catalytic

$TiO_2/V_2O_5/WO_3/MoO_3$
Fe/Cr-Oxide
Zeolite

Reduction

NO_x with $NH_3 \longrightarrow N_2 + H_2O$

Note:

- High efficiency (up to > 90%)
- Final products N_2 and H_2O

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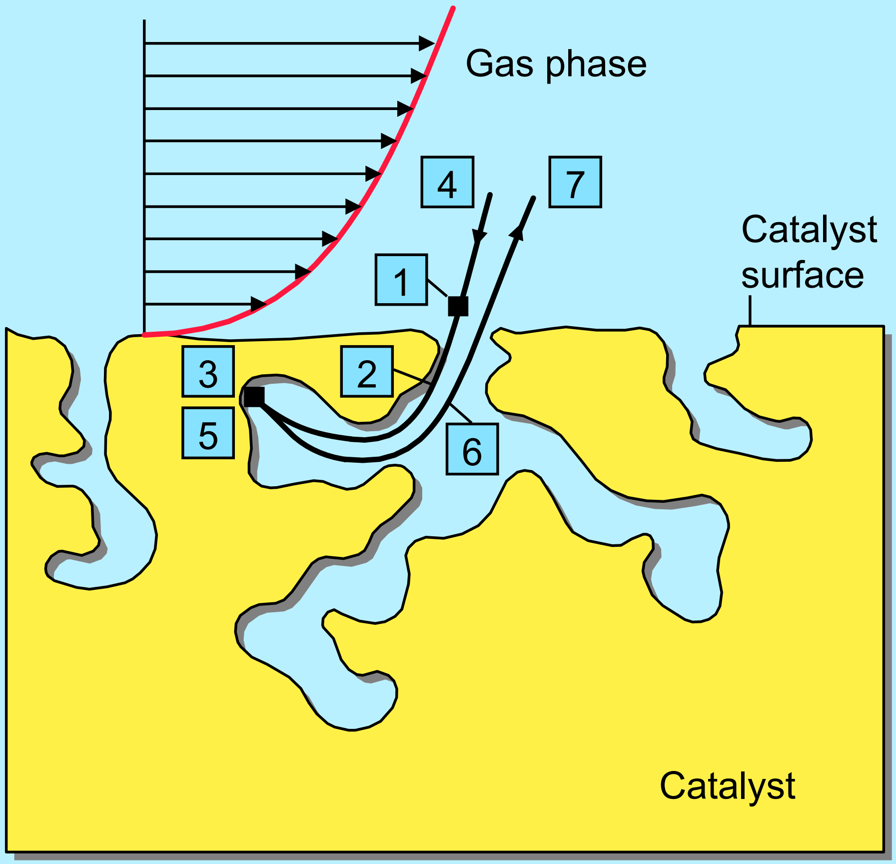
Selective Catalytic Reduction - Principles
Some possible side reactions

$4\ NH_3 + 3\ O_2$	-->	$2\ N_2 + 6\ H_2O$	Not observed
$4\ NH_3 + 5\ O_2$	-->	$4\ NO + 6\ H_2O$	At 1050 - 1200 °C
$4\ NH_3 + 7\ O_2$	-->	$4\ NO_2 + 6\ H_2O$	
$2\ NH_3 + 2\ O_2$	-->	$2\ N_2O + 3\ H_2O$	Not observed
$2\ NH_3 + 8\ NO$	-->	$5\ N_2O + 3\ H_2O$	

$2\ SO_2 + O_2$	-->	$2\ SO_3$	Limited by catalyst selection composition and design
$NH_3 + SO_3 + H_2O$	-->	NH_4HSO_4	Limited by catalyst design
$NH_4SO_4 + NH_3$	-->	$(NH_4)_2SO_4$	and operating temperature
$Hg^0 + 2HCl + ½O_2$	-->	$HgCl_2 + H_2O$	Limited by Halogen content

Selective Catalytic Reduction - Principles
Reaction Kinetics



1. External diffusion of NH_3 to catalyst surface
2. Internal diffusion of NH_3 into the catalyst pore
3. NH_3 adsorption on the active centers
4. NO diffusion from gas phase to adsorbed NH_3
5. Reaction of NO and NH_3 to N_2 and H_2O
6. Desorption from N_2 and H_2O to catalyst surface
7. Diffusion of N_2 and H_2O into gas phase

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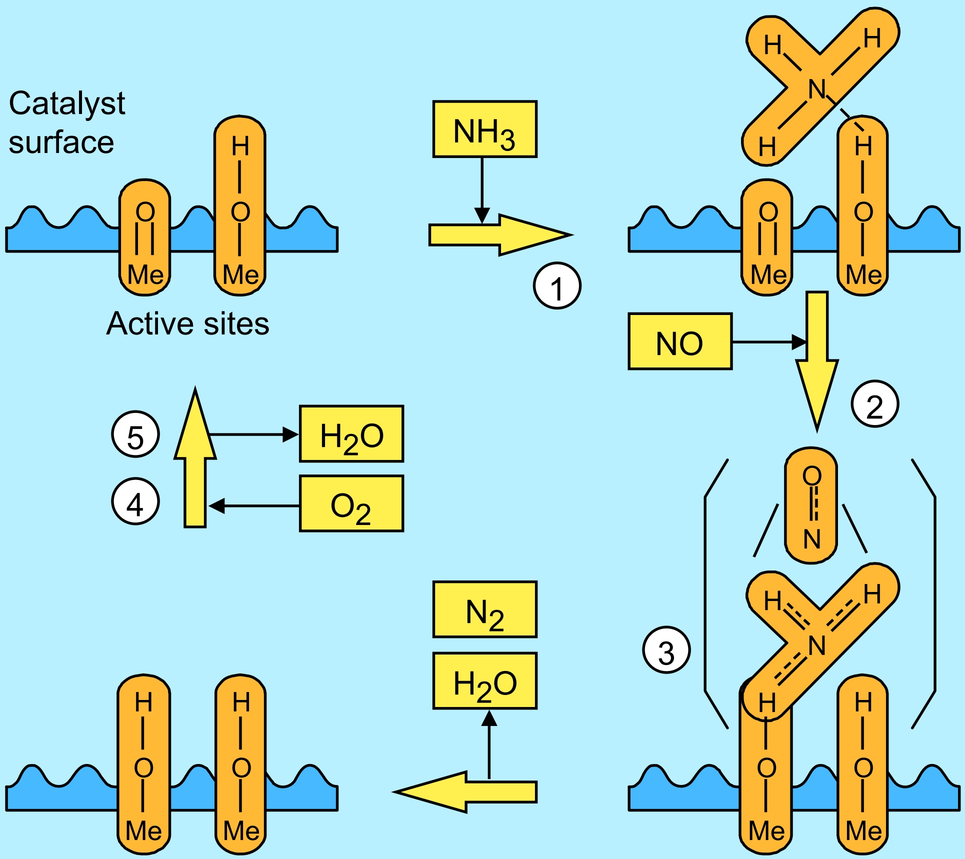
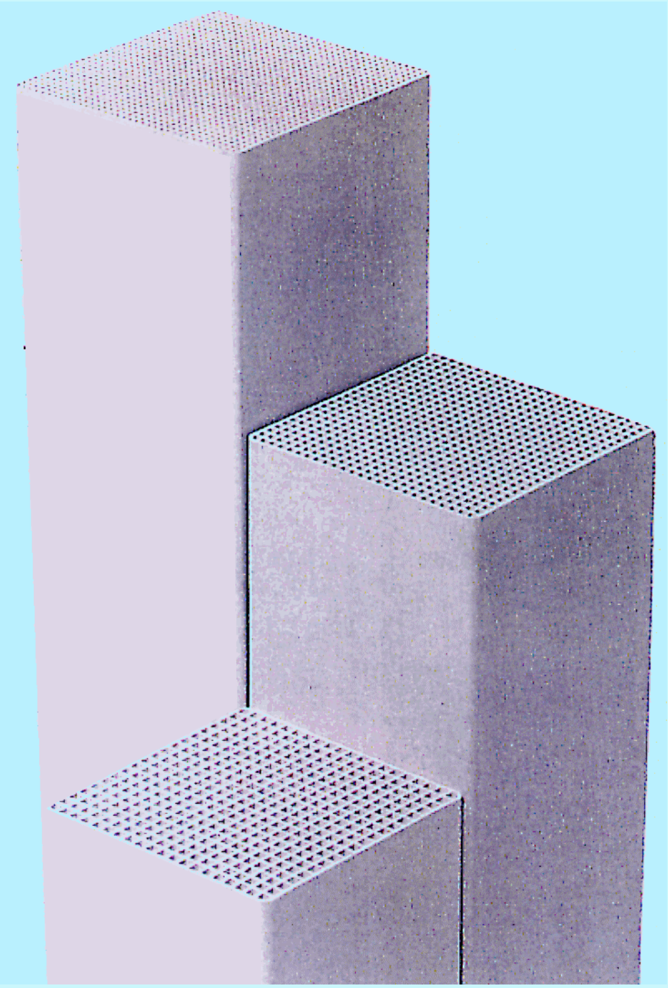
Selective Catalytic Reduction - Principles
Reaction Mechanism



1. NH_3 adsorption on catalyst surface
2. NOx diffusion to adsorbed NH_3
3. Reaction on catalyst surface (reaction rate is determining step)
4. Oxidation of the metal hydroxides
5. Regeneration of active sites by oxidation

Plate and Honeycomb



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Fuels

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- Gas
- Oil
- Bituminous Coal (EB)
- Sub-bituminous Coal (PRB)
- Lignite
- Pet Coke
- Bio-residue
    - Renewable (wood, straw, peat)
    - Residue (sewage sludge, municipal waste, meat and bone meal)
- Tire derived fuel
- Blends and campaigns

Coal

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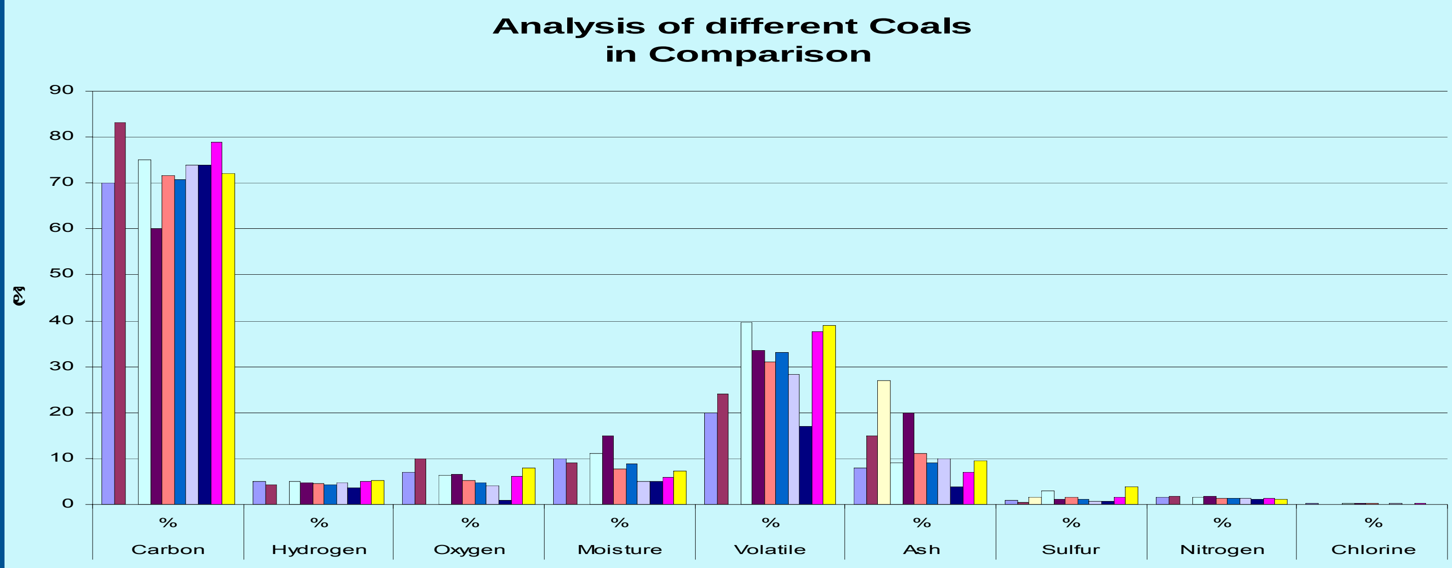
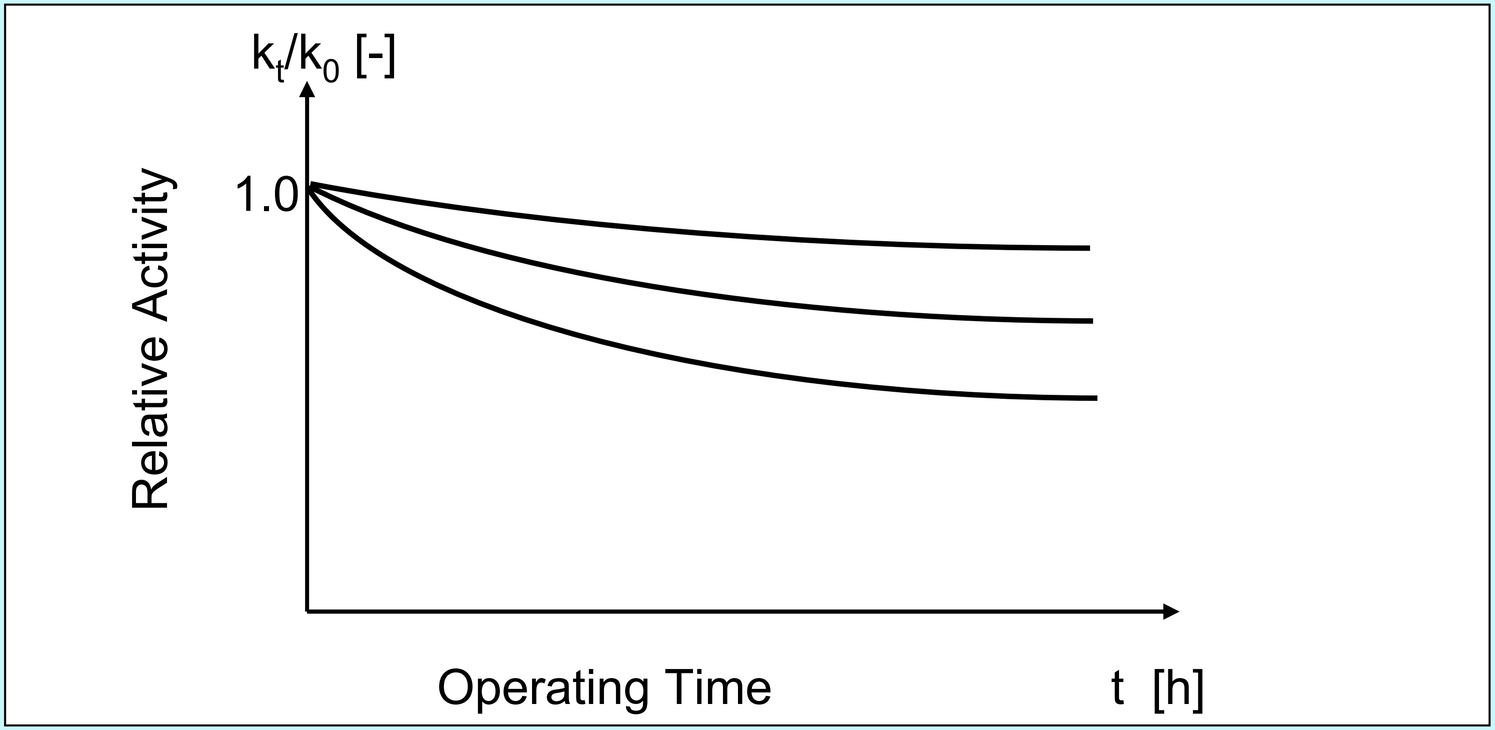


Deactivation

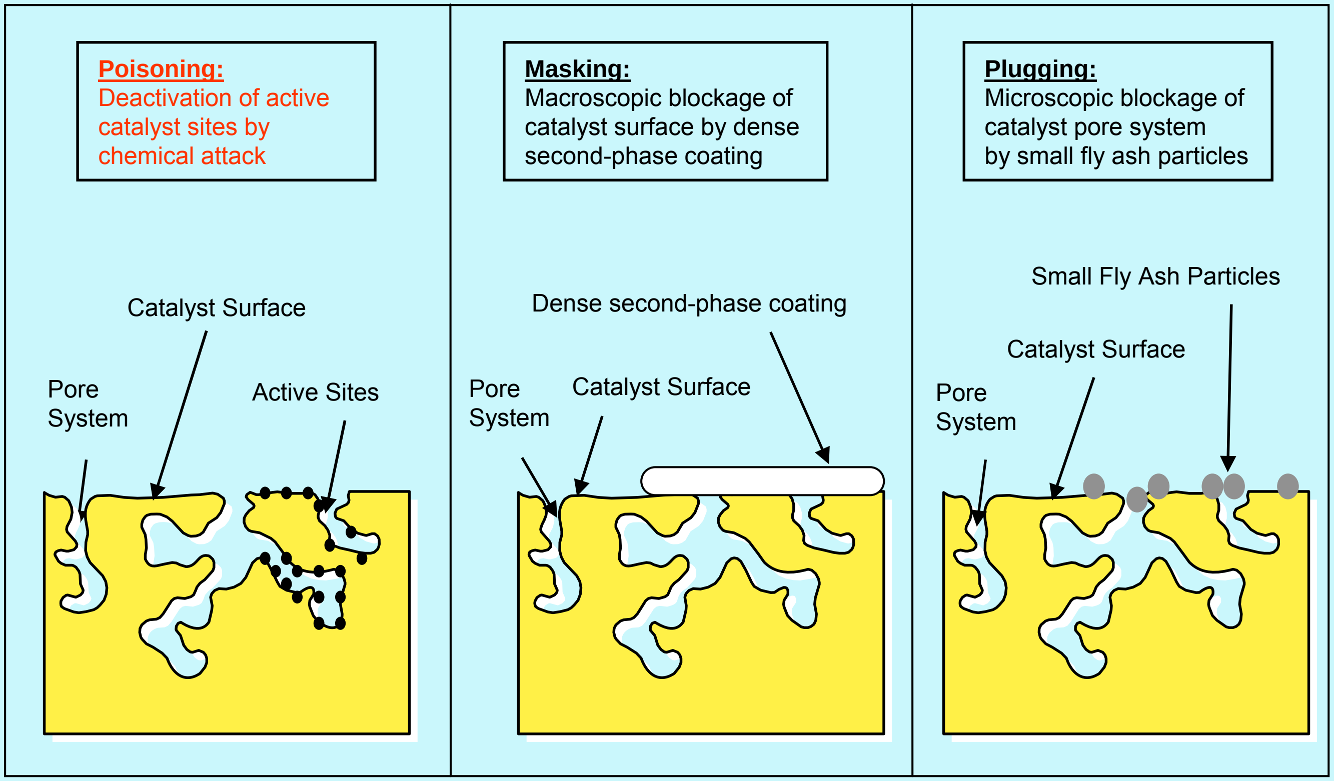


$$k/k_o = e^{-\lambda \cdot t}$$

Deactivation

- Deactivation by plugging, fouling and pore clogging (ash, ABS)
- Deactivation by erosion (Al2O3, SiO2, FeS)
- Deactivation by thermal sintering
- Deactivation by poisonous flue gas constituents
- Deactivation due to damage caused by abnormal operations (frequent cold start-ups, tube leaks,…)

Deactivation mechanisms



Poisoning

- Catalytic activity: Brønsted sites on catalyst surface
- Poisoning: basicity of metal oxide deposits
- Boiler temperature 2500 F and higher
- Combustion and ash physics & chemistry
    - Volatility during and after combustion;
    - Condensation of volatiles on fly ash; smaller particles are richer in volatiles
    - Transport
    - Deposition, adhesion, exchange

Deactivation: poisoning

- Trace elements (Heavy and Base Metals): As, V, Cr, Se, …
- Alkali and Alkaline metals K, Na, Ca, Mg, …
- Biomass - Phosphorous, P-compounds

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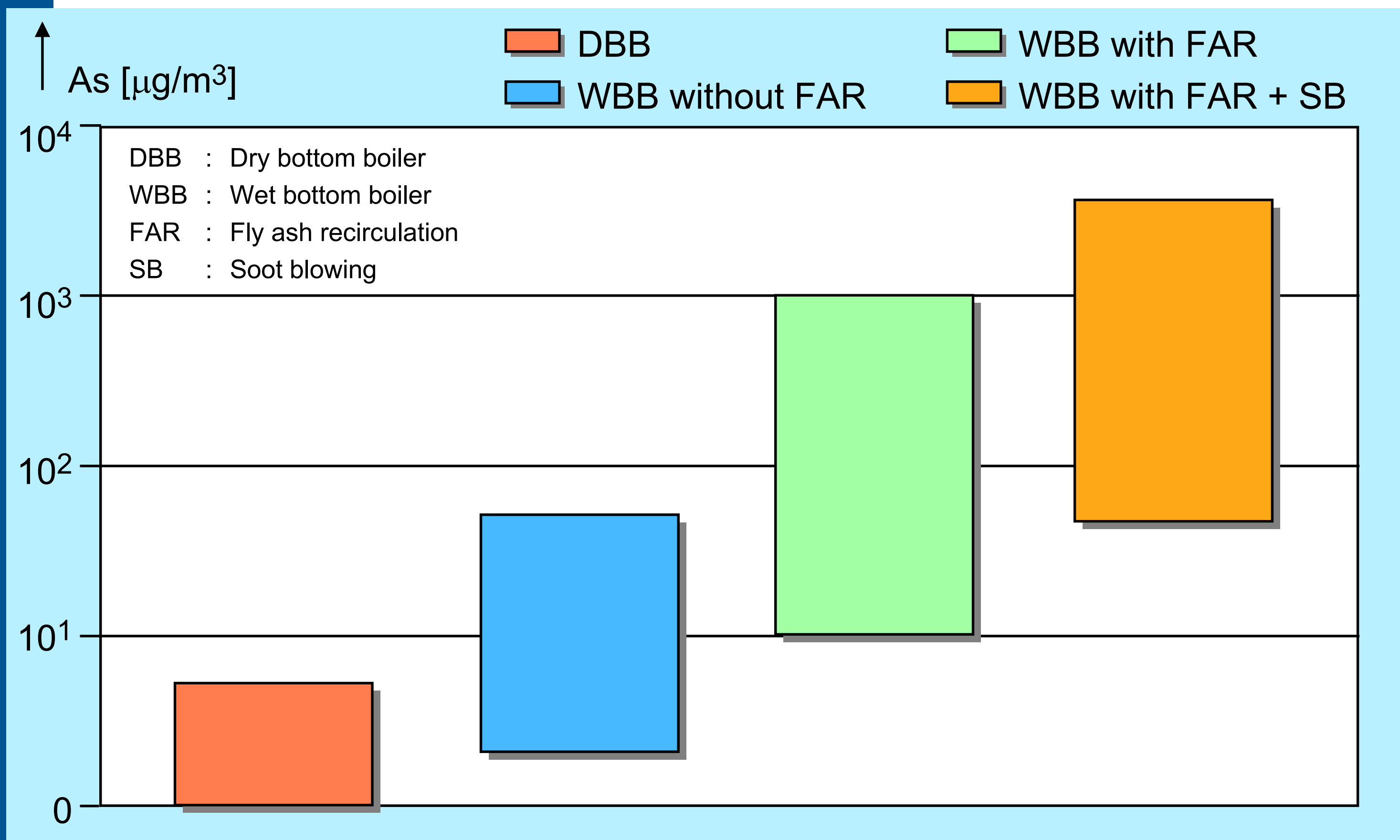
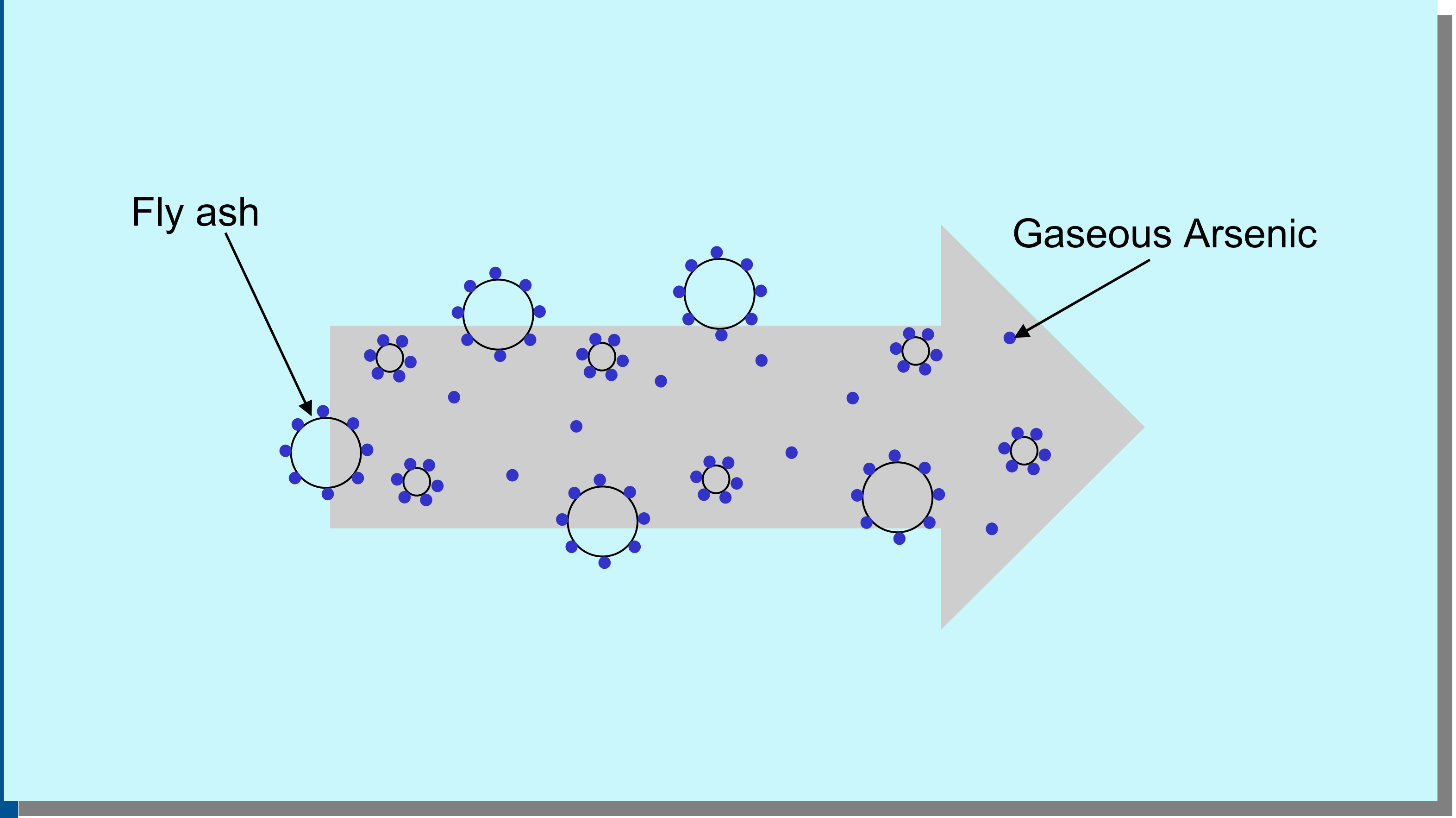
Poisoning: Heavy/Base Metal trace elements

- As
- V (deposits cause extra bisulfate formation)
- Cr, Se, Ni, Fe, …

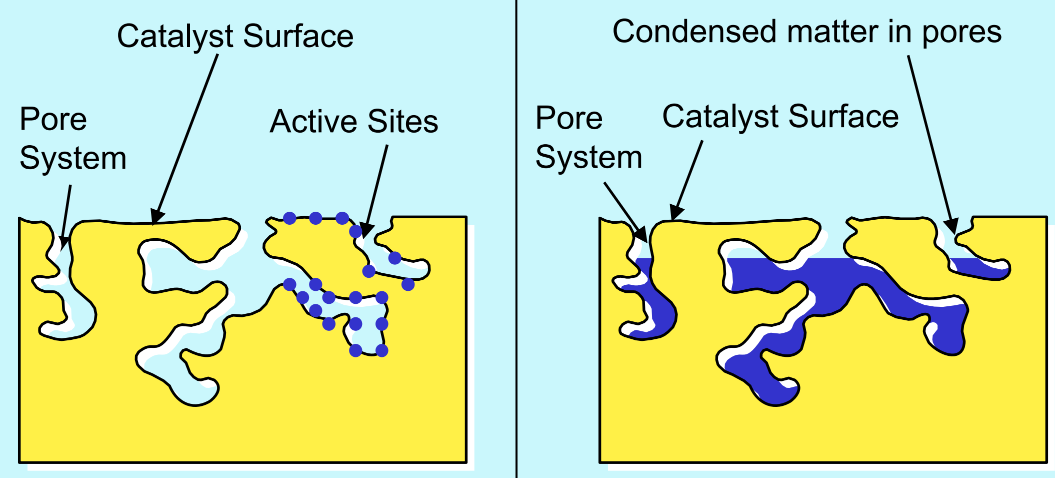
Arsenic: flue gas concentrations for various boiler types



Arsenic



Arsenic



Poisoning (chemical deactivation)

Pore condensation (physical deactivation)

Arsenic

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Physical catalyst deactivation:

- Gaseous arsenic molecules are much smaller than catalyst pores
- Pore condensation of arsenic starts in small pores (Kelvin equation)
- Small catalyst pores are essential for catalyst activity (surface area)
- Pore condensation stops when pore filling reaches equilibrium conditions (k_t/k_0 plateau)

Arsenic

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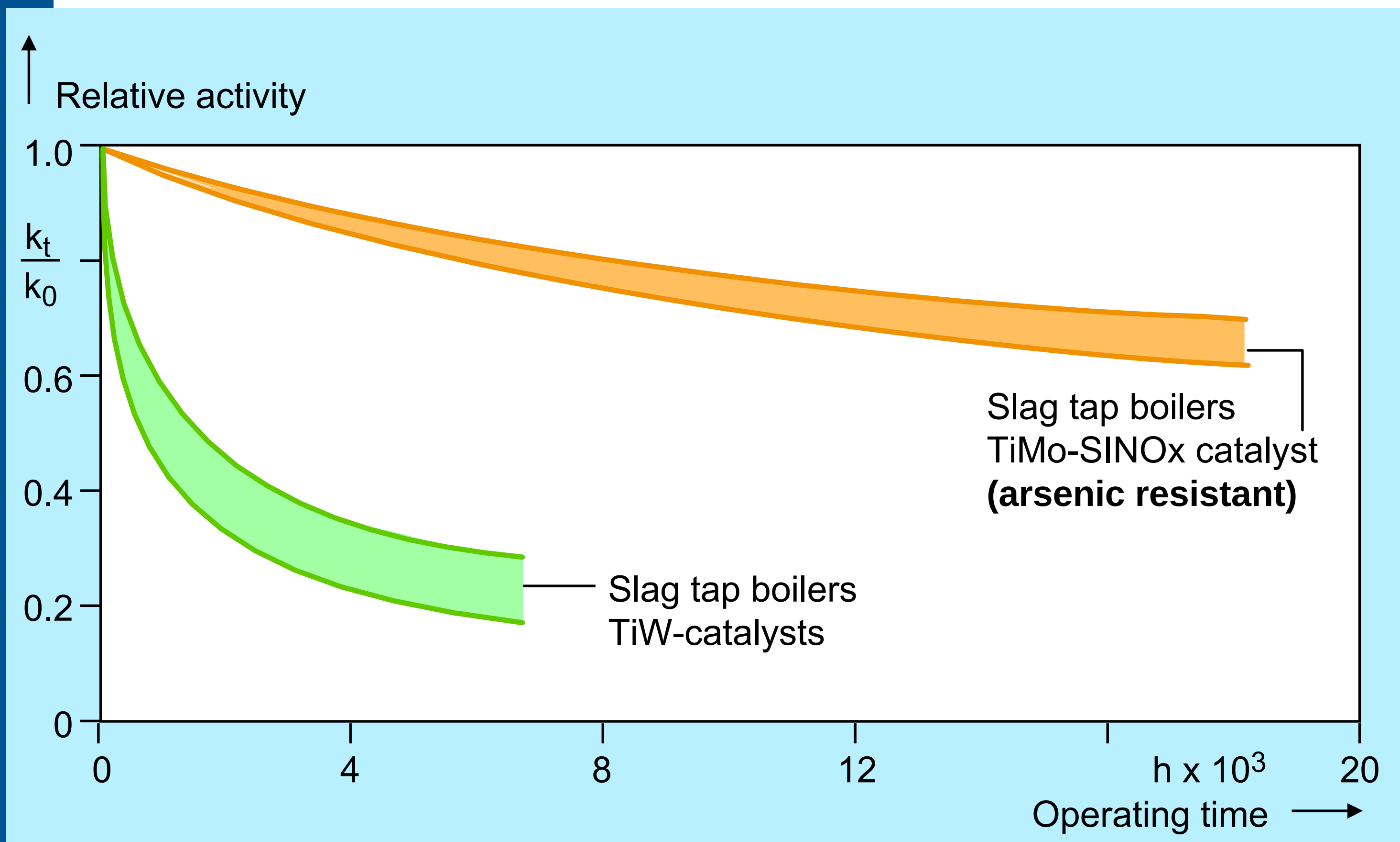
Chemical catalyst deactivation:

- Gaseous arsenic molecules react with active V_2O_5 sites to form stable, non-catalytic compounds (TiW catalysts)
- Chemical deactivation risk remains until all active sites are deactivated
- MoO_3 is more reactive with As than V_2O_5
- The addition of MoO_3 protects the active V_2O_5 sites against deactivation (TiMo catalysts)
- The addition of MoO_3 slightly modifies the pore structure; at same pore distribution Mo catalyst shows better As resistant

Mitigation: Arsenic Resistant Catalyst - TiMo



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Arsenic mitigation

Calcium Oxide in coal

• Gaseous arsenic levels in flue gas are a function of the calcium oxide concentration in coal

• Fly Ash >950F – Calcium Arsenate formation:

$$3CaO + As_2O_{3(g)} + O_2 \quad \text{----------->} \quad Ca_3\,(AsO_4)_2$$

•The catalyst deactivation rate will be slower with CaO concentrations greater than 1% in coal (~2-3$^+$% in ash)

• Argillon studied the correlation between As and CaO concentrations, boiler type and fly ash re-circulation to be able to accurately predict gaseous arsenic concentrations in flue gas

• Knowledge of these factors proved to be vital for assessing the catalyst deactivation rate for design and volume calculations

Arsenic mitigation

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CaO in fly-ash

- levels
  - •Arsenic <5 ppm : no CaO in ash required
  - •Arsenic 5 -10 ppm: a minimum of 1 % of CaO is required in the ash
  - •Arsenic 10 -20 ppm: a minimum of 3 % of CaO is required in the ash
  - •Arsenic >20 ppm: a minimum of 4 % of CaO is required in the ash
- limestone injection, limitations on fuels and more frequent catalyst replacements are expensive mitigation tools

Vanadium

Heavy fuel oil, Pet Coke, some Coals

- Oil, Pet Coke – (high) sulfur, Vanadia – blue plumes, corrosion
- Vanadium content >20-30 ppm up to >>100 ppm
- Oil history: Canal Station
- Vanadyl Sulfate $VOSO_4$ (and V_2O_5) on fly ash sticking to the catalyst surface
- Deposits cause increased SO_2 to SO_3 conversion
- Deposits on catalyst ($VOSO_4$) react with active sites
- Coal Vanadia: 10-180 ppm; no increase of SO_2 oxidation noticed – attributed to fly ash absorption of gaseous V_2O_5

Vanadium mitigation

Fuel oil, Pet Coke, some Coals

- Oil additives (Mg), boiler additives, flue gas additives (CaO)
- Start with "full" load of lower activity/low SOx cat and remove/add layers of catalyst over time
- "Vanadia resistant catalyst" – barrier layer
- Pet Coke: blend with EB

Vanadium

Vanadia sweet spot: East Coast plant 700MW, PC fired boiler, Low Dust (after ESP)

- EB, 40-50 ppm Vanadium
- Catalyst installed in 2001

Various base metal and heavy metal trace elements

Volatility, concentration, fly ash – poisons list covering the usual suspects, but every situation is different

- Pb, Zn, Hg, Cd
- Cr - Cat Crackers - pore blockage (Cr2O3)
- Ni, Sb, Se

Alkali and Alkaline metals: poisoning

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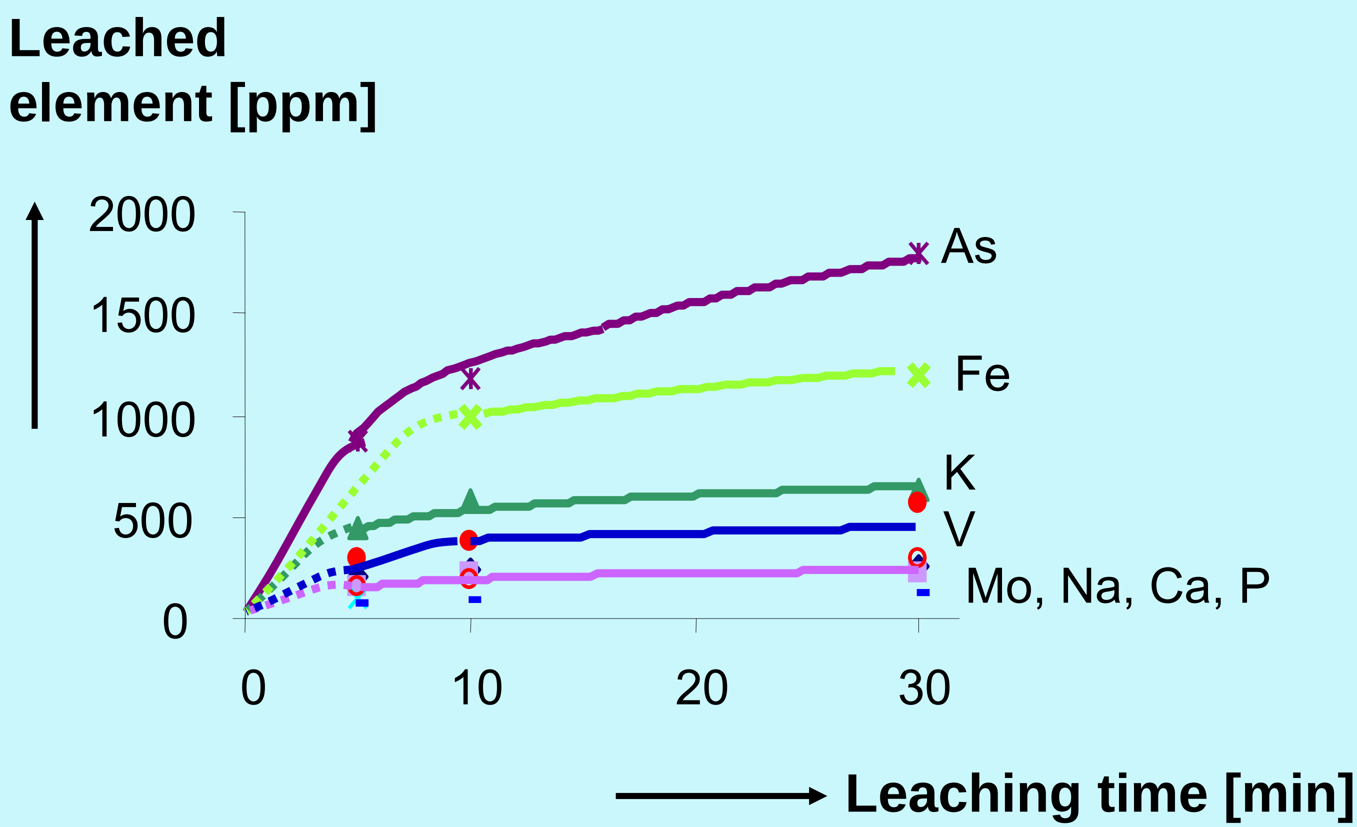
- K, Na, but also Earth metals like Ca and Mg are chemical poisons (literature)
- Na, K in ash > 0.5-1% (acid) soluble
- Usually low concentrations of Cs, Li, Ru, Ba, Sr
- Water soluble salts of biggest concern – water soluble is highly mobile – ion exchange reaction with active sites:
    - Alkali-Vanadium compounds [Martin et al., 1988].
    - poisoning effect of (free) CaO is less than that of other alkaline metal oxides [Chen et al. (1990)]
- Operations: boiler water
- EB: mainly non-water soluble alkalines
- PRB, Northern Lignite, straw, wood, peat: more soluble, greater risk of poisoning

Leaching of plate-type catalyst in lab-scale tests (acidic solution)



Leaching of plate-type catalyst in lab-scale tests (basic solution)

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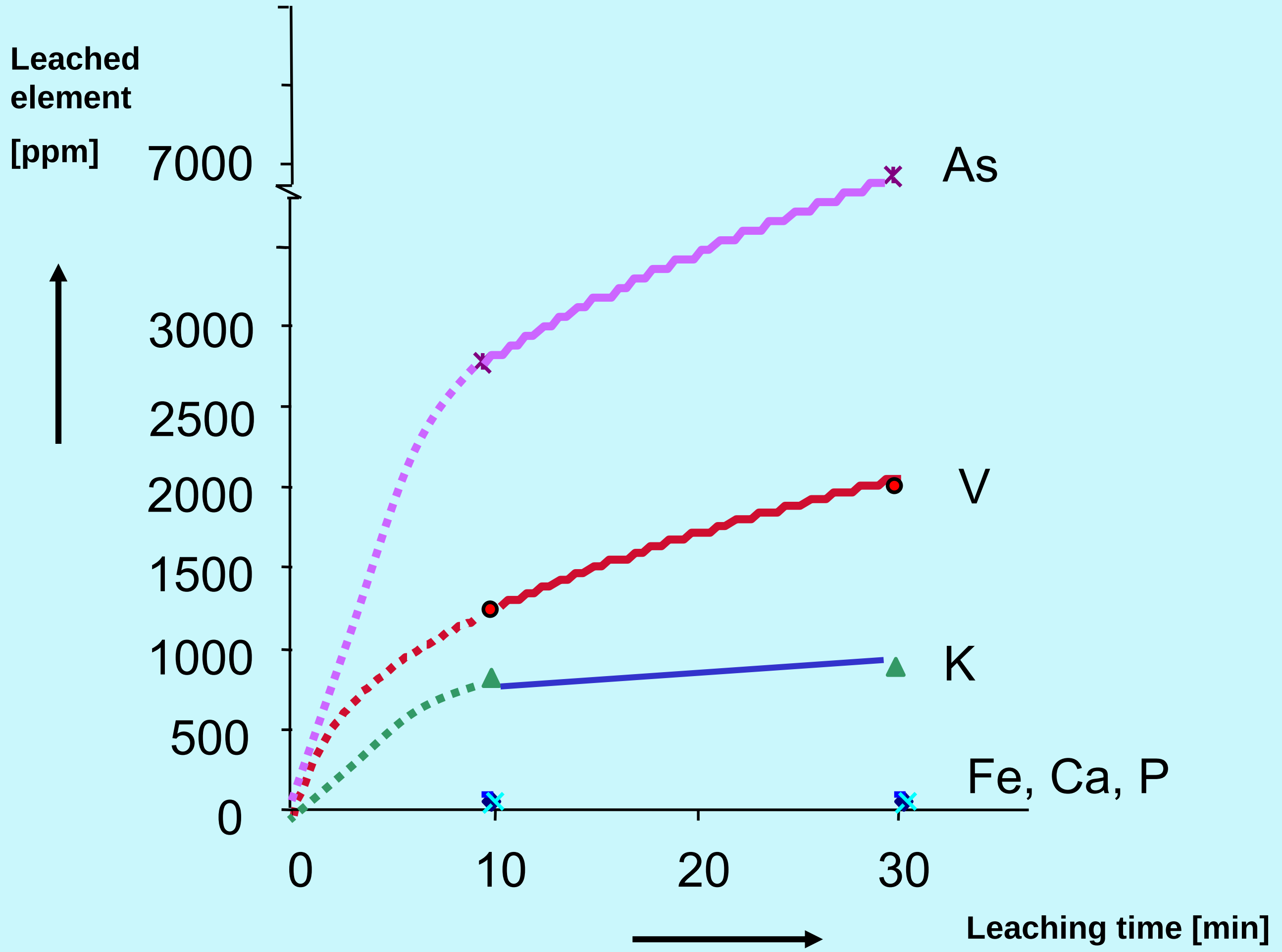
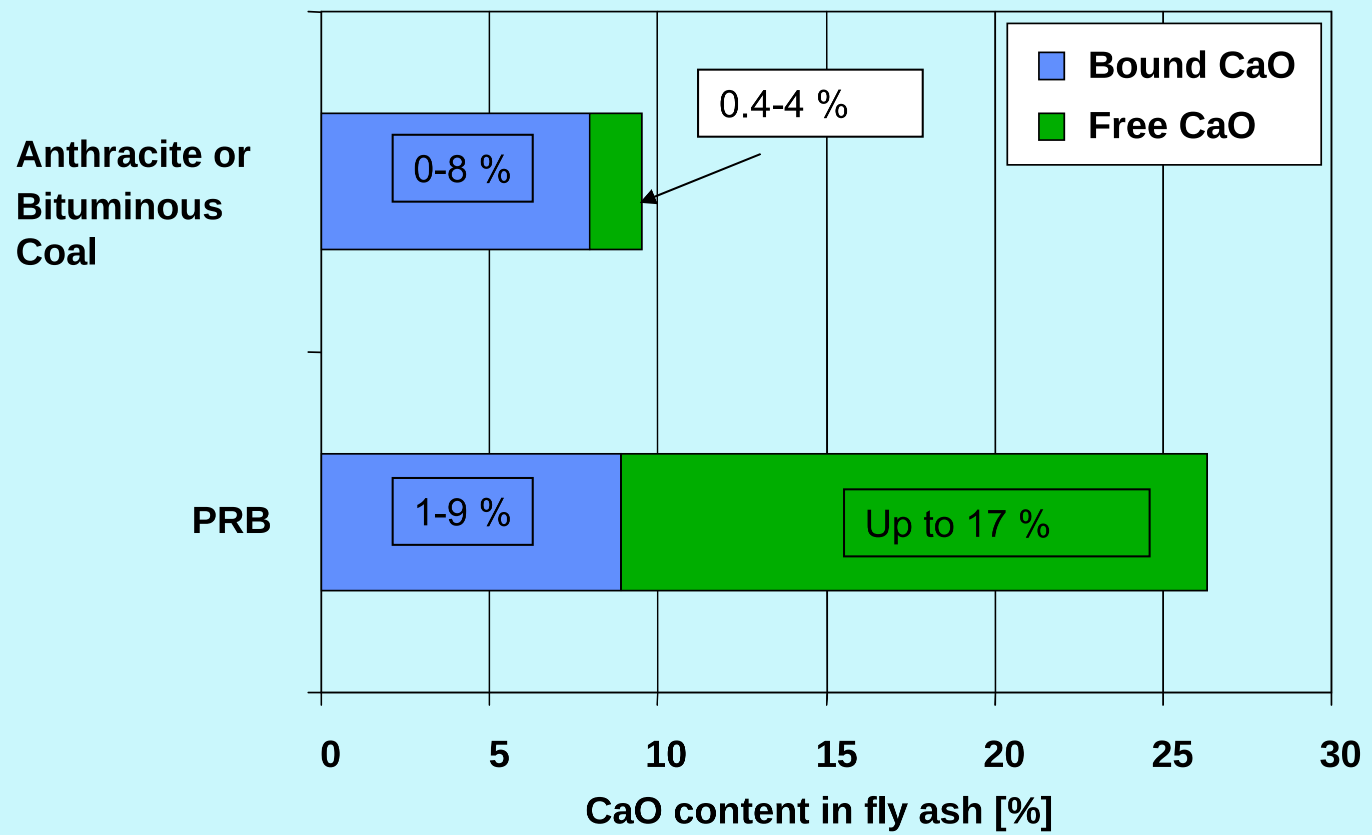


Free CaO in fly ash



Alkali and Alkaline metals: Mitigation

- avoid dew point conditions
- reversible reaction – Alkali culprits can “in principle” be washed out

Phosphorus, Biomass

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Biomass (co-firing), wood, bone meal, grain, sewage sludge

- Biomass worse in Alkali than coal
- Biomass worse in Phosphorus than coal
- High Phosphorus concentrations in Meat & Bone Meal, sewage sludge, grain
- Co-firing up to 5% increases deactivation (ref. University of Stuttgart: activity decrease 30% in 4000h for 4% MBM)
- Ca and Na-Phosphates, surface layer
- Phosphorus in Coal

Mitigation

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Biomass (co-firing), wood, bone meal, grain, sewage sludge

- Co-firing % of total fuel
- Catalyst volume
- Dew point conditions

Operational considerations

- Boiler water, tube leaks (water, alkali)
- Cold Start ups and dew point conditions in general
- (Partial) bypass

Conclusions

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- Deactivation by poisoning a predominant factor in case of:
  - High Arsenic concentrations
  - High Alkali concentrations
  - High Phosphorus concentrations
- Mitigation:
  - Avoid dew point conditions
  - Special catalyst types
  - Additional catalyst volume
  - Reagent addition to fuel or flue gas
- Pamper your $catalyst$

Questions?