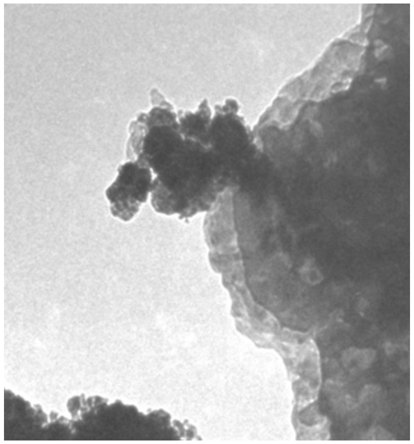
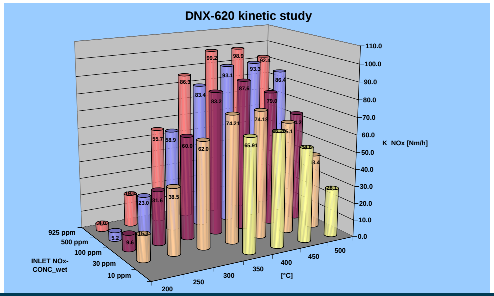
Reinhold Environmental Ltd.

2010 NOx-Combustion Round Table & Expo Presentation

February 8 & 9, 2010 ***Chattanooga, TN***





New Catalyst Advancements

Joakim Reimer Thøgersen

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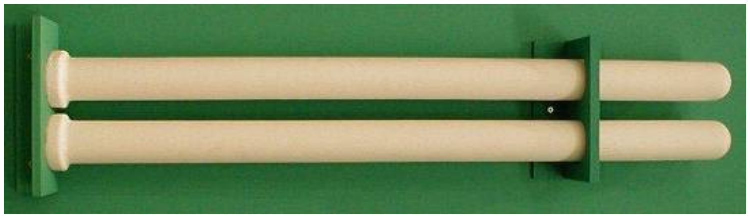

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Table of contents

- Market trends
- Trends in SCR DeNOx applications
  - Automotive SCR
  - Coal fired power plants
  - Gas turbines
  - Marine Vessels
- New catalyst developments
  - Cerafil TopKat
  - Monolith catalysts

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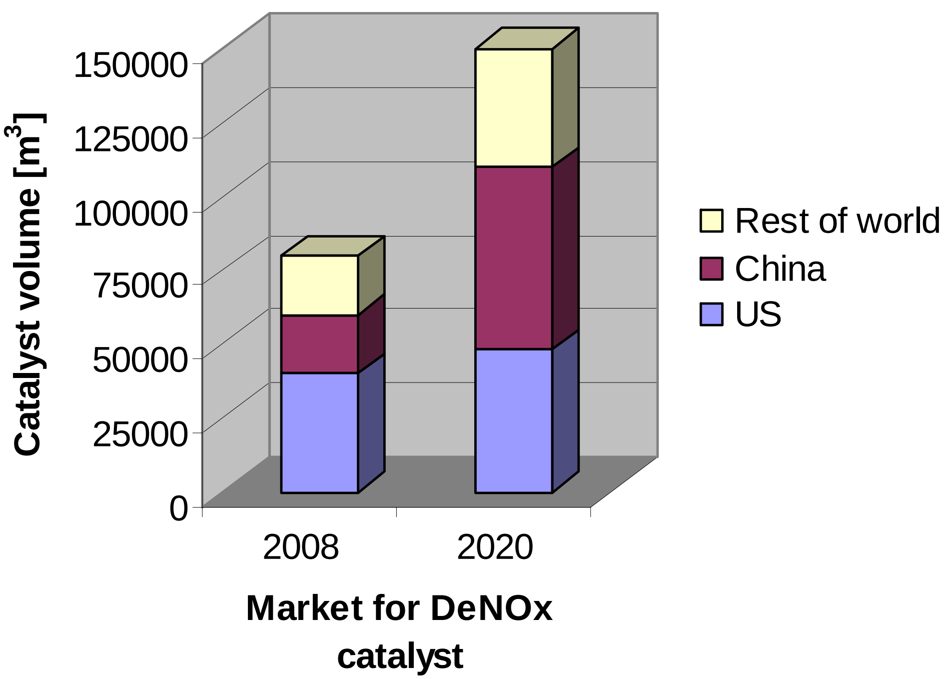
SCR DeNOx market trends

- 2008 world market: 80,000 m^3
- 2020 world market: 150.000 m^3



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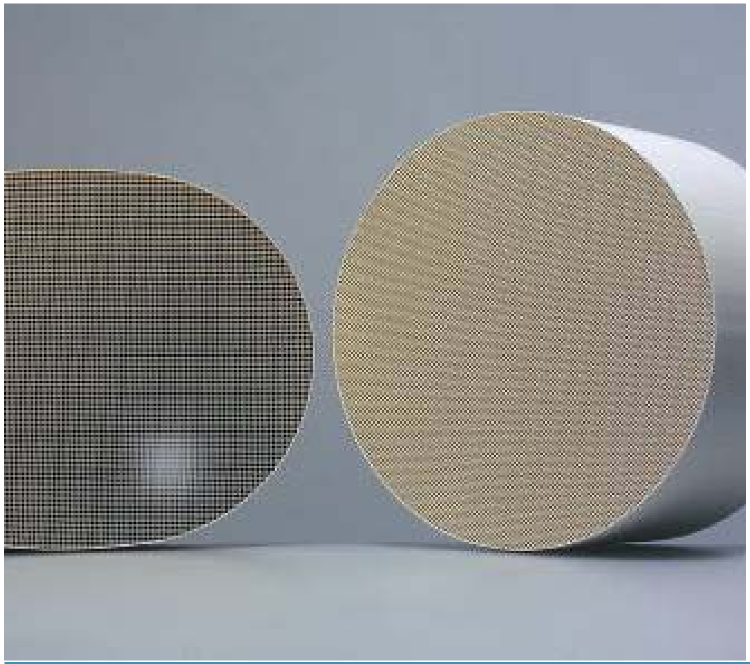

Automotive SCR

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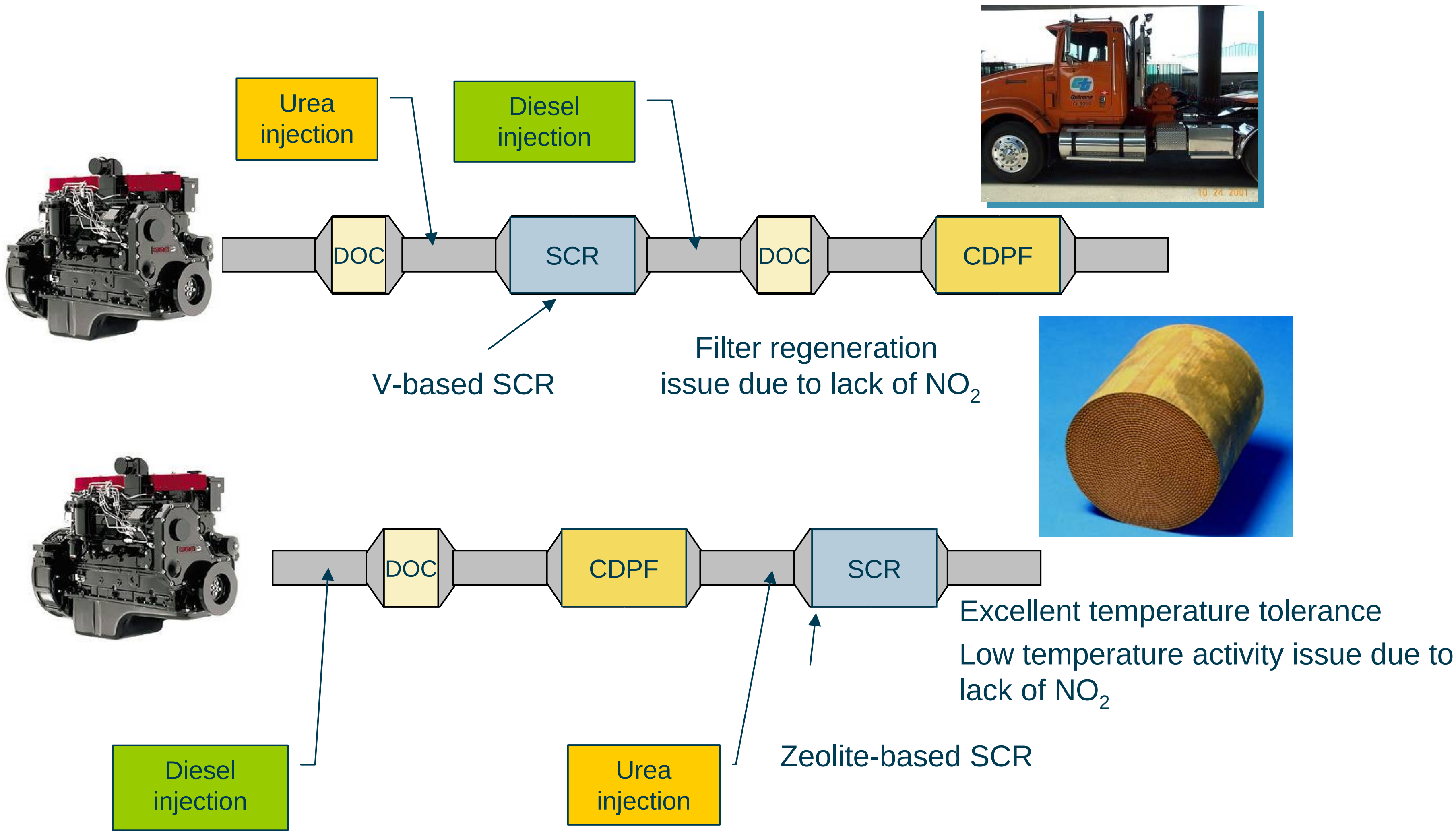
Diesel emission system for Euro VI
Removal of HC, CO, PM and NOx



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Coal-fired power plants

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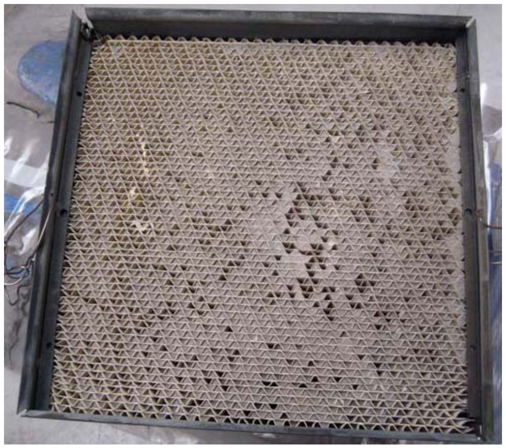
Coal-fired power plants

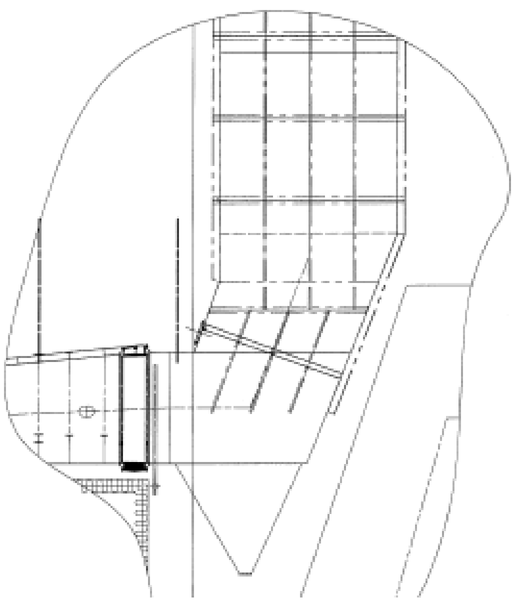
- Biomass co-firing
  - SCR catalyst deactivation
- Hg capture
  - SCR catalyst impact on mercury chemistry. CAMR legislation under review in the US.
- Reduced load operation
  - Minimum temperature issues
- SCR in low rank coal fired units
  - Catalyst deactivation
- Catalyst regeneration

Studstrup Power Station

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

Coal/Straw co-firing at Studstup Power Station - Plugging due to incomplete burn-out of straw





Ref: Dong Energy, Expperts 2008 Brussels

SCR biomass-fired boilers

Utility	Plant	Power	Fuel	%DeNOx	Start-up
High dust					
Dong Energy	Avedøre	400 MW	Oil, wood, gas	80	2001
Vattenfall	Uppsala	120 MW	Peat	75	2005
Corn Fiber	Ft. Dodge IA		Wood	82	2008
Sierra Power	Terra Bella, CA	7 MW	Wood	65	2008
Low dust					
SUEZ Energy	Bethlehem, NH	16 MW	Wood	46	2008
SUEZ Energy	West Ossipee, NH	22 MW	Wood	46	2008
Synterprise	GlobalSolutions TN		Wood	35	2008
United Corrstack	Community Power NH		Wood	81	2008
Corrugated Services	Forney, TX		Wood	75	2008

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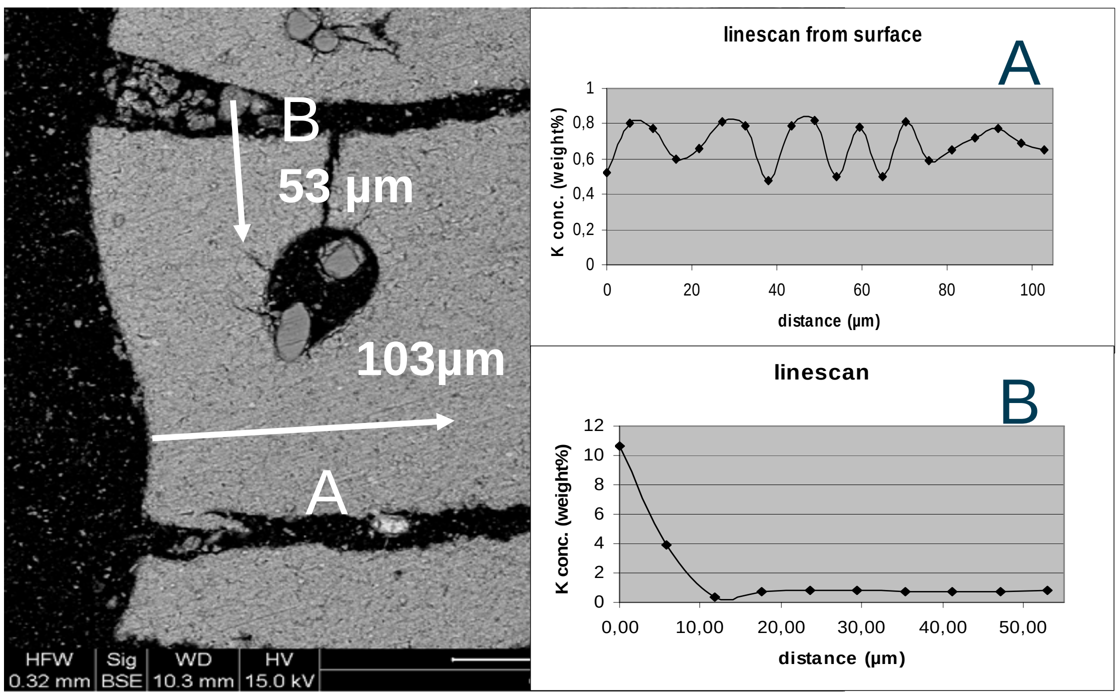
Biomass and SCR deactivation

- Evaporation of potassium in the furnace
  - Deactivation rate: PC boilers > CFB boilers > Grate fired boilers
- Nucleation of fine sub-micron potassium aerosols
- Deposition of aerosols on catalysts surface
- Diffusion into catalyst by surface diffusion
- Reaction with active site



4600 service hours at Nassjö Power Plant (Accelerated test)

Quantitative chemical analysis shows 7000 ppmw potassium

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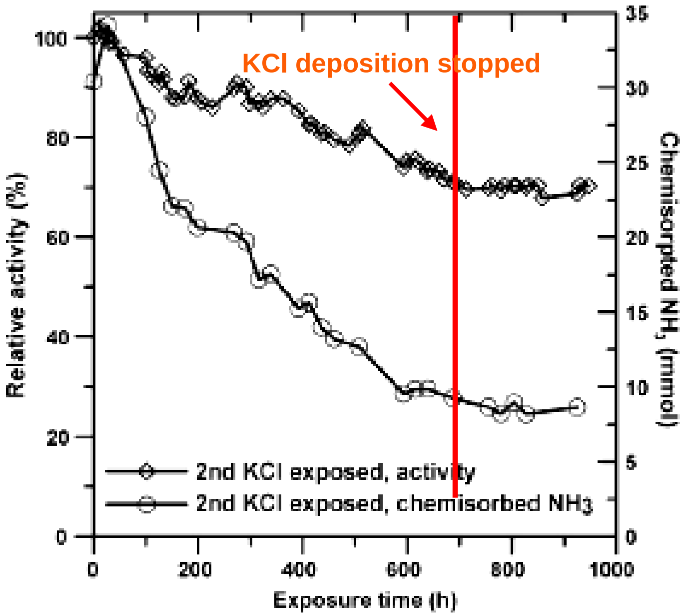
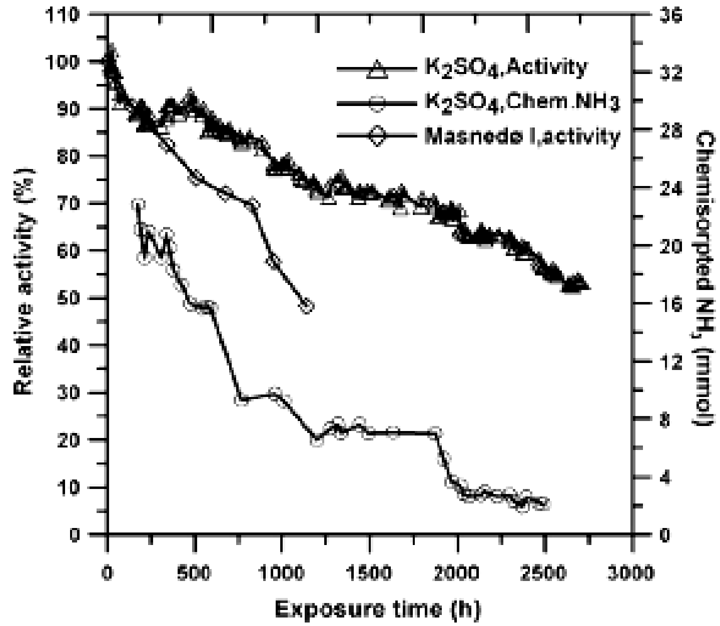
Bench scale experiments with furnace Injection of potassium salt solutions

KCl aerosols



Deactivation 50%/1000h

K_2SO_4 aerosols



Deactivation 30%/1000h

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

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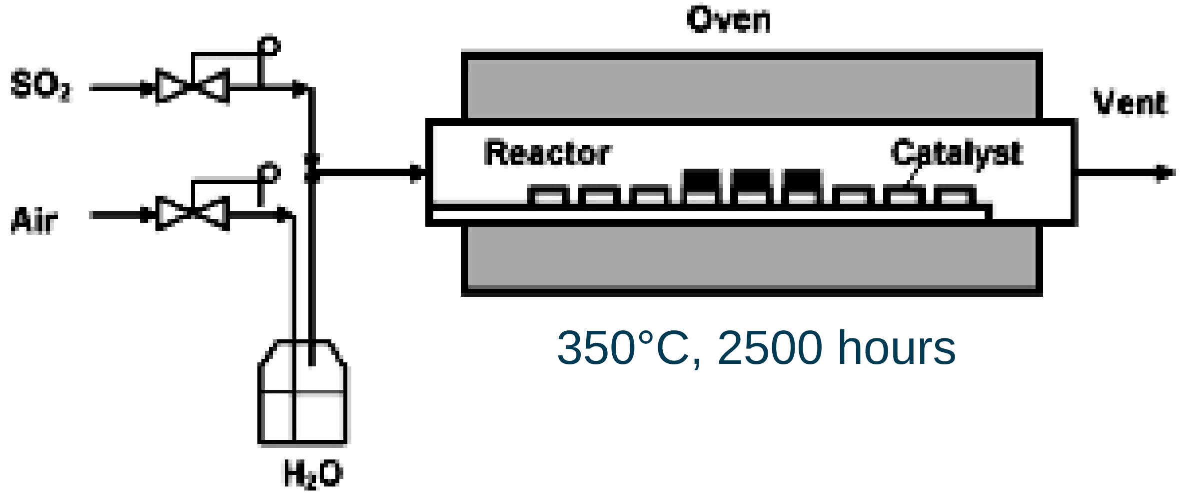
Zheng et. al Applied catalysis B: Environmental

KCl powder deactivation experiments

- Commercial grade KCl placed on catalyst
  - Almost no deactivation of center catalyst
  - No deactivation of downstream catalyst
- Fly ash recovered from full scale reactor placed on catalyst
  - No deactivation observed



350°C, 2500 hours

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Zheng et. al Applied catalysis B: Environmental

Typical deactivation rates (high dust)

100% straw	50%/1,000h
Wood-fired PC fired boiler	60%/10,000h
Wood-fired CFB boiler	45%/10,000h
Wood-fired Grate fired boiler	25%/10,000h
Peat-fired boiler	30%/10,000h
Coal-fired boiler	10%/10,000h
Heavy fuel oil	5%/10,000h
Gas-fired boiler, low dust	2%/10,000h

Note: Depends on specific fuel composition

Mercury emissions from coal-fired power plants

- Mercury occurence: 0.1-1 ppmw Hg in coal
- Mercury emissions: 1-20 µg Hg/Nm3 (<2 ppbv)
- Coal fired power plants are the largest single source of anthropogenic mercury emissions in the US
  - Appr. 48 tons of mercury was emitted annually in 1999

Speciation and fate of mercury

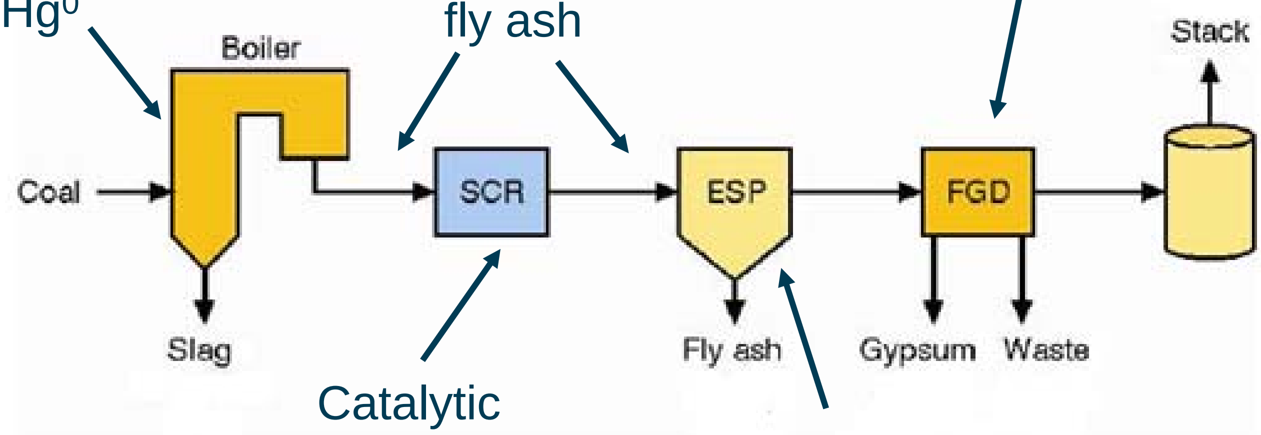
- Mercury species: Hg^0, Hg^{2+} and Hg^p
- Speciation determines capture in pollution control devices

Homo- and heterogeneous oxidation of Hg^0

Absorption of Hg^{2+} in scrubber

Evolution of Hg from coal as Hg^0

Adsorption of Hg^0 and Hg^{2+} on fly ash



Catalytic oxidation of Hg^0 to Hg^{2+}

Removal of Hg adsorbed on fly ash

Heterogeneous oxidation of Hg^0 in FF

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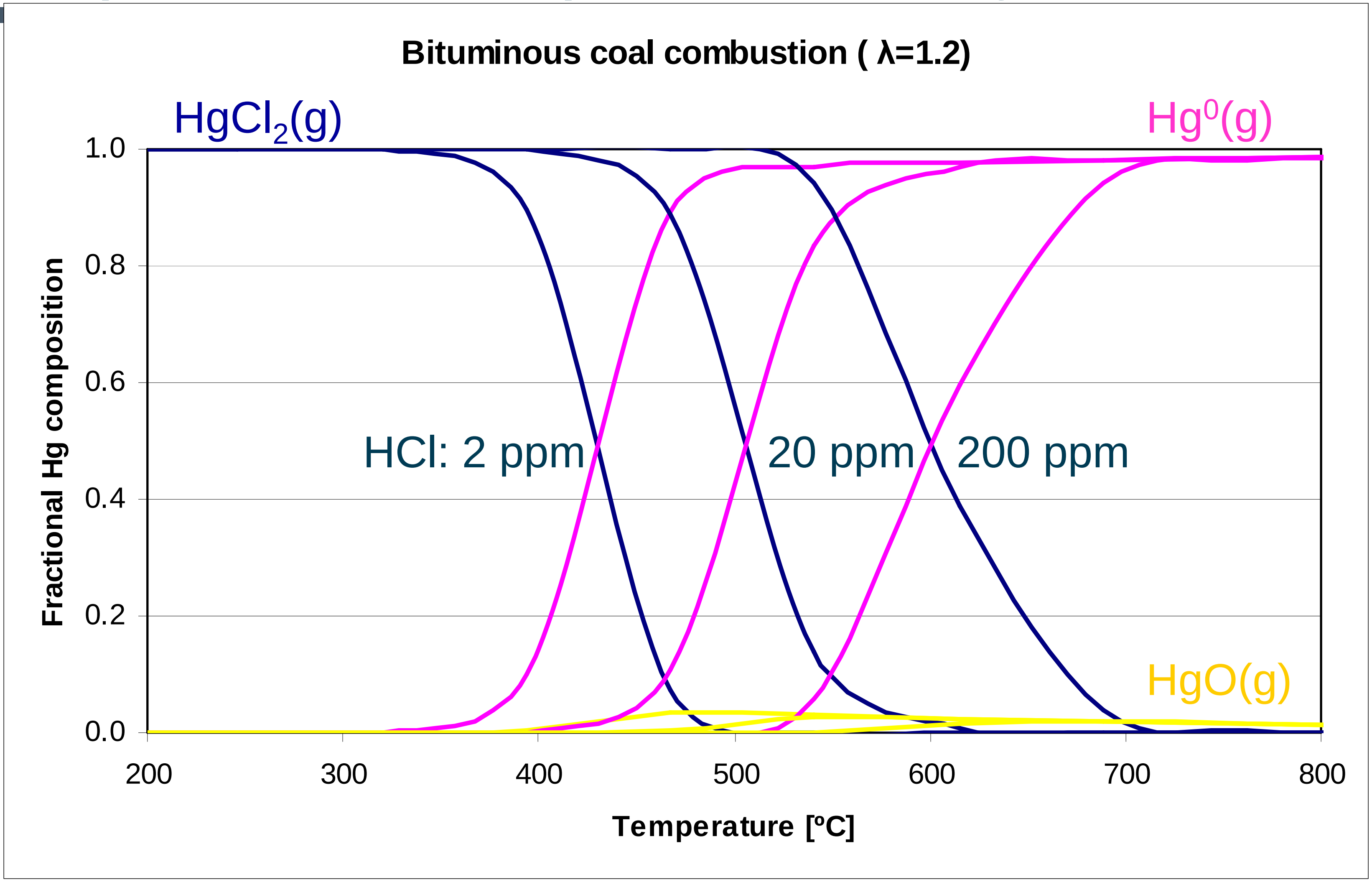
Equilibrium composition of Hg (gas-phase)



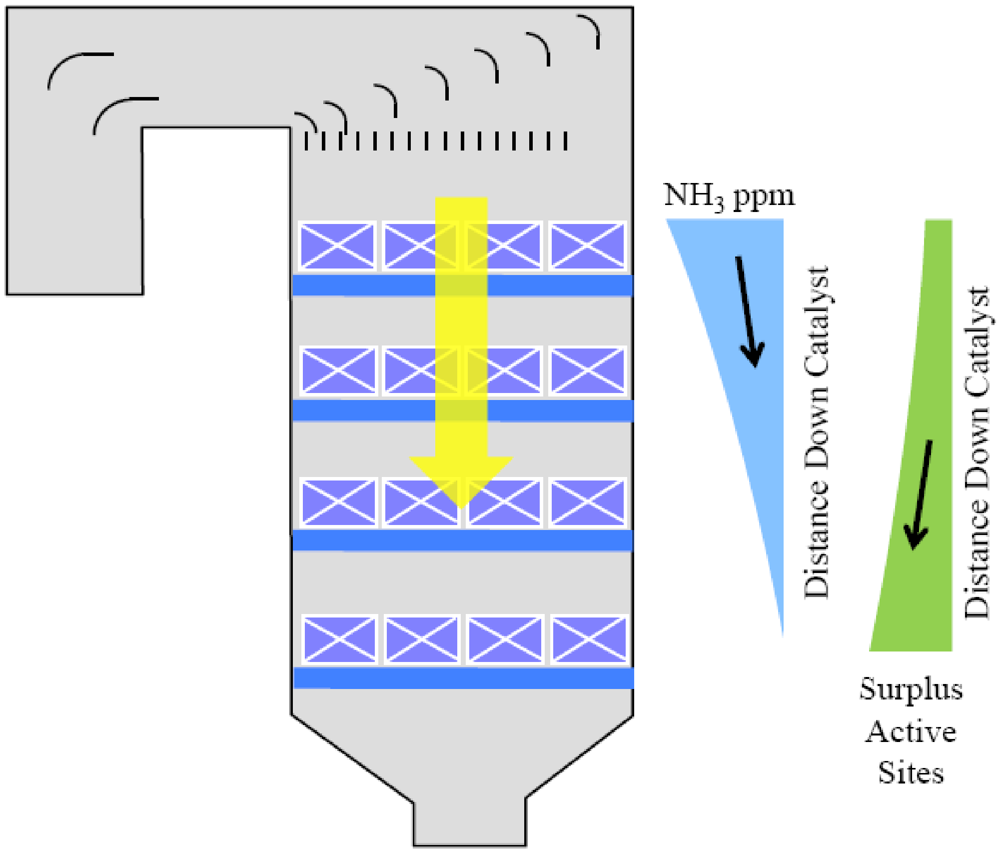
Mercury chemistry – upstream of APCDs

Important parameters

- Unburned carbon in the fly ash
- Presence of acid gasses
- Time - temperature history
- Calcium

These will be a function of coal rank/type and operating conditions - including type of burner and air/fuel ratio.

Mercury oxidation across SCR catalyst



Two proposed reaction mechanisms:

1. Hg^0 adsorbs to the surface and reacts with gaseous HCl
2. HCl adsorbs to the surface and reacts with gaseous Hg^0

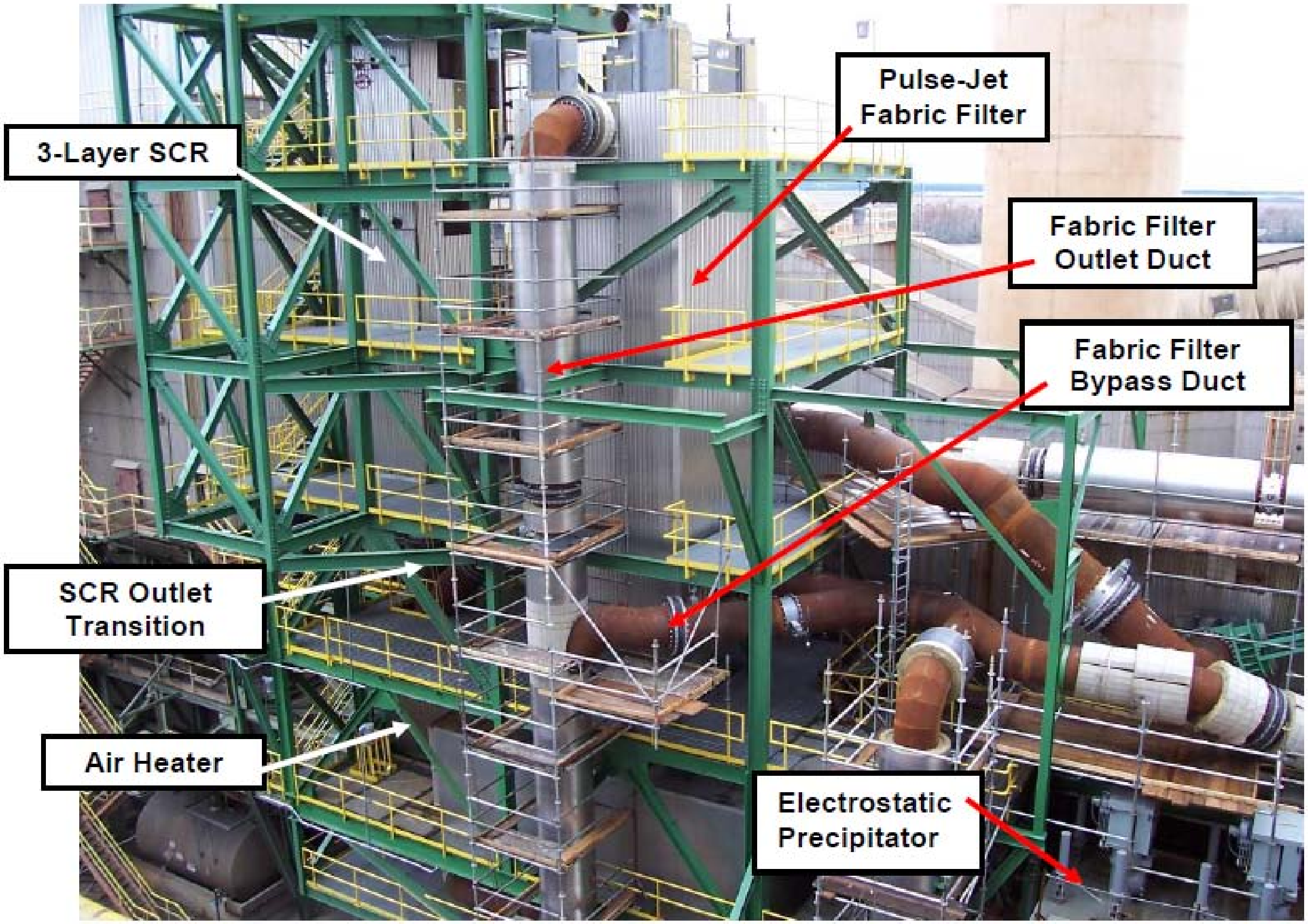
The adsorbing specie competes with NH_3 for binding on V_2O_5

Plant Crist (Pensacola) Parametric Study

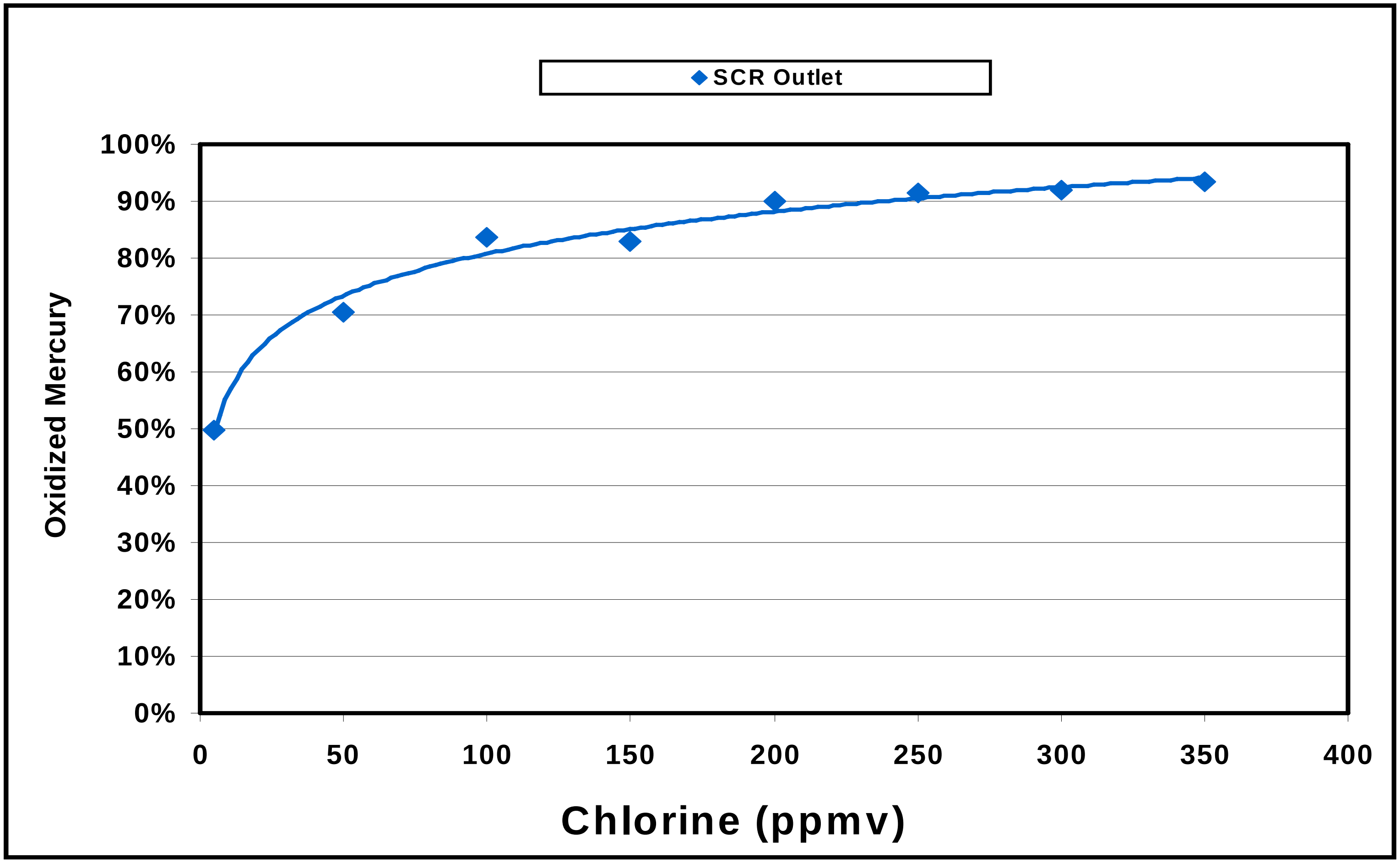
- MRC (Mercury Research Center), Sponsored by EPRI
- 5 MW equivalent slipstream facility
- 8 m^3 catalyst in two layers, type DNX-664
- Bituminous Coal: Low chlorine Columbian coal

  - Low baseline conversion (40%)
- Effect of Temperature, HCl, (HBr), NH_3, Flow rate

Mercury Research Center



Effects of Chlorine on SCR Catalyst Hg Oxidation
Averaged from 4 tests



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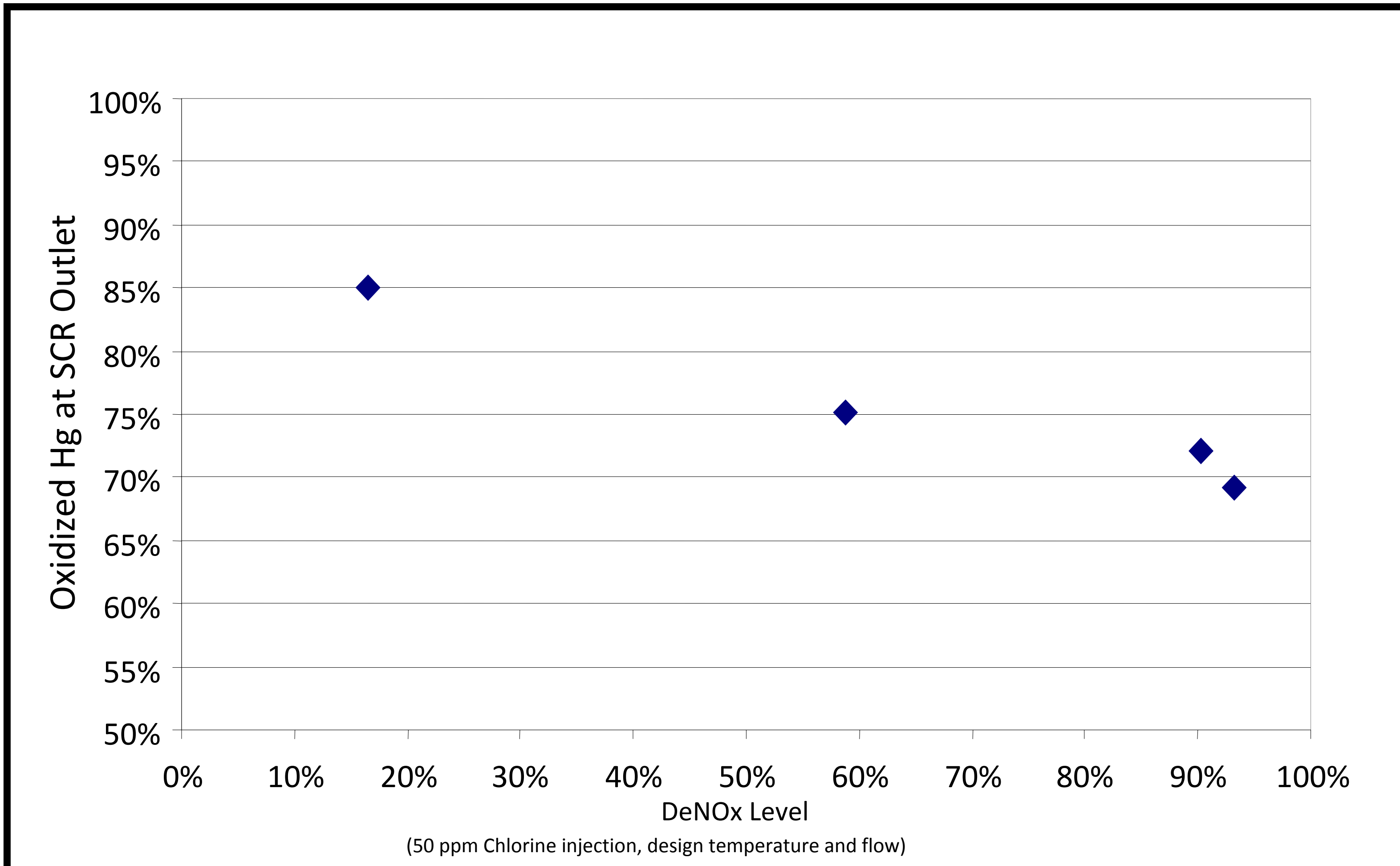
Ammonia and Chlorine Effects



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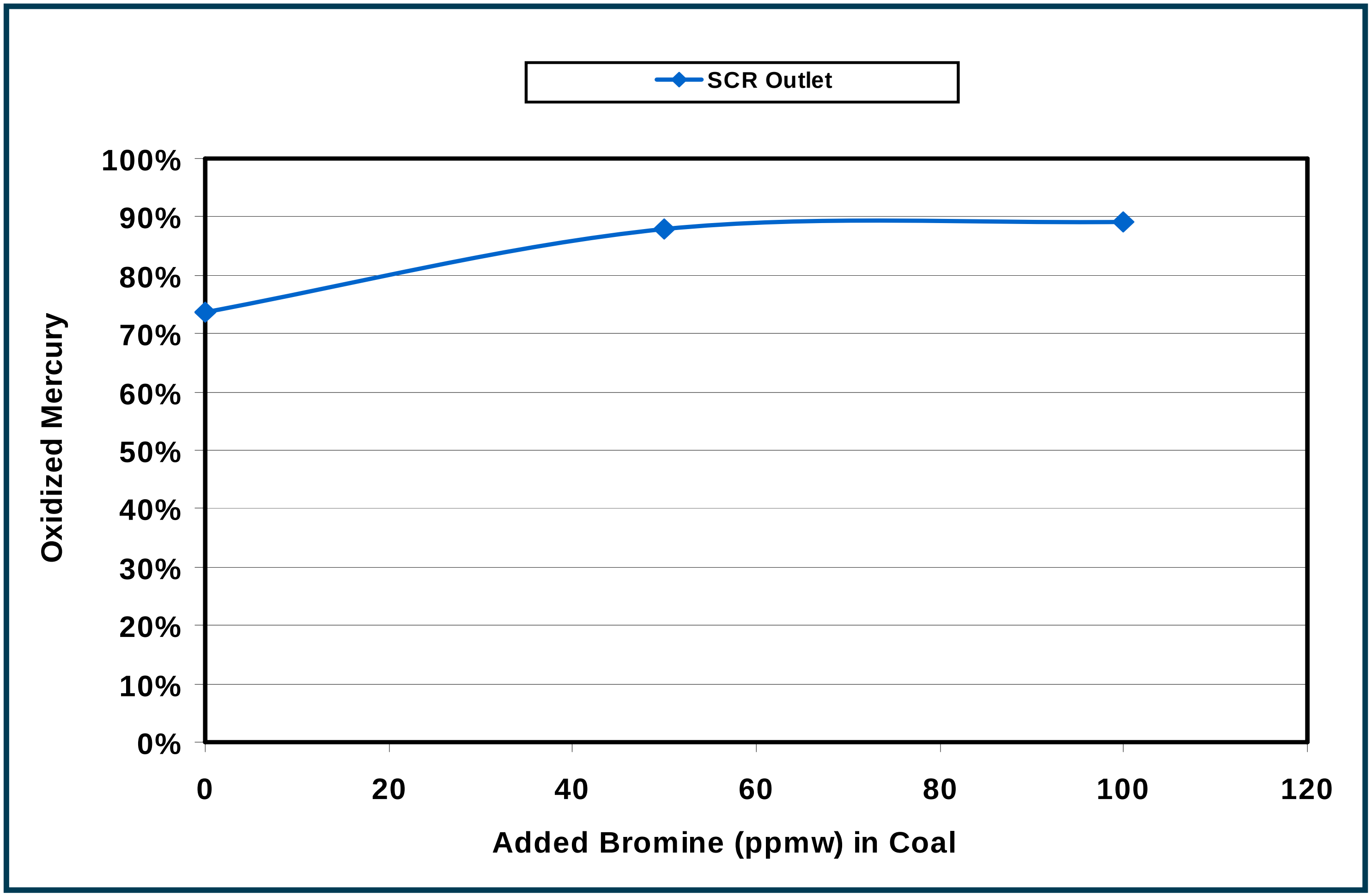
Effects of Bromine on SCR Catalyst Hg Oxidation
Averaged from 4 tests



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Modeling of reactions across the SCR

- $4\ NO + 4\ NH_3 + O_2 \rightarrow 4\ N_2 + 6\ H_2O$
- $Hg^0 + 2\ HCl + \frac{1}{2}\ O_2 \rightarrow HgCl_2 + H_2O$
- Model
  - Plug flow in the monolith channel
  - Gas film diffusion
  - Pore diffusion and reaction in the wall
  - Reactions via Eley-Rideal mechanisms

Two alternative Eley-Rideal mechanisms

- Adsorption of Hg

$$-r_s = \frac{k \cdot K_{Hg} \cdot P_{Hg} \cdot P_{HCl}}{1 + K_{NH3} \cdot P_{NH3}}$$

- Adsorption of HCl

$$-r_s = \frac{k \cdot K_{HCl} \cdot P_{Hg} \cdot P_{HCl}}{1 + K_{NH3} \cdot P_{NH3} + K_{HCl} \cdot P_{HCl}}$$

Day-to-day variation is explained by inlet speciation

- Conversion:

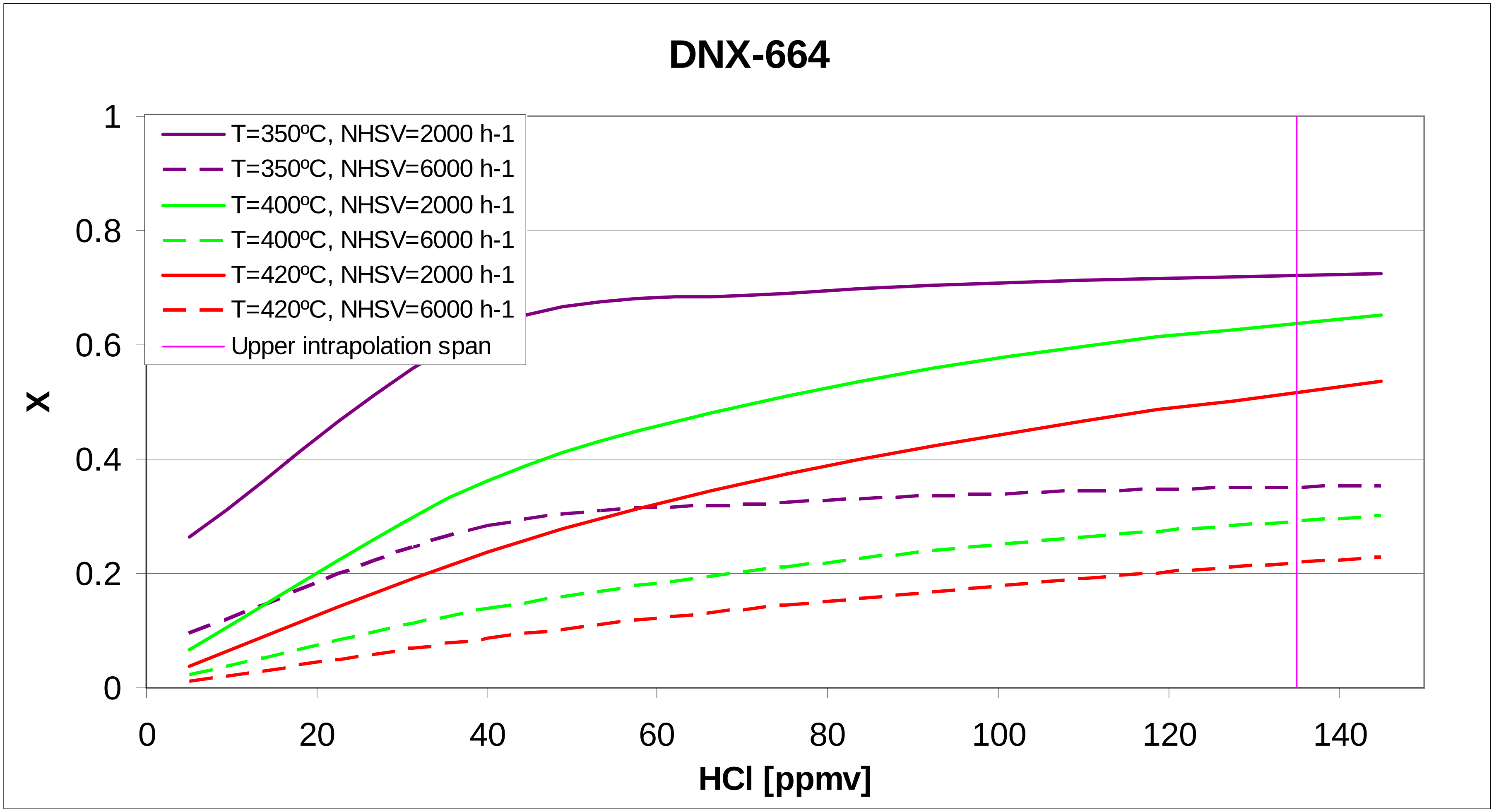
$$X = \frac{\Delta Hg^{0}}{Hg^{0}(in)}$$

- Outlet speciation:

$$y^{2+}(out) = y^{2+}(in) + X \cdot y^{0}(in)$$

$$where \quad y^{i}(out) = \frac{Hg^{i}(out)}{Hg^{Total}}$$

Modeling Hg^0 Oxidation across HCl



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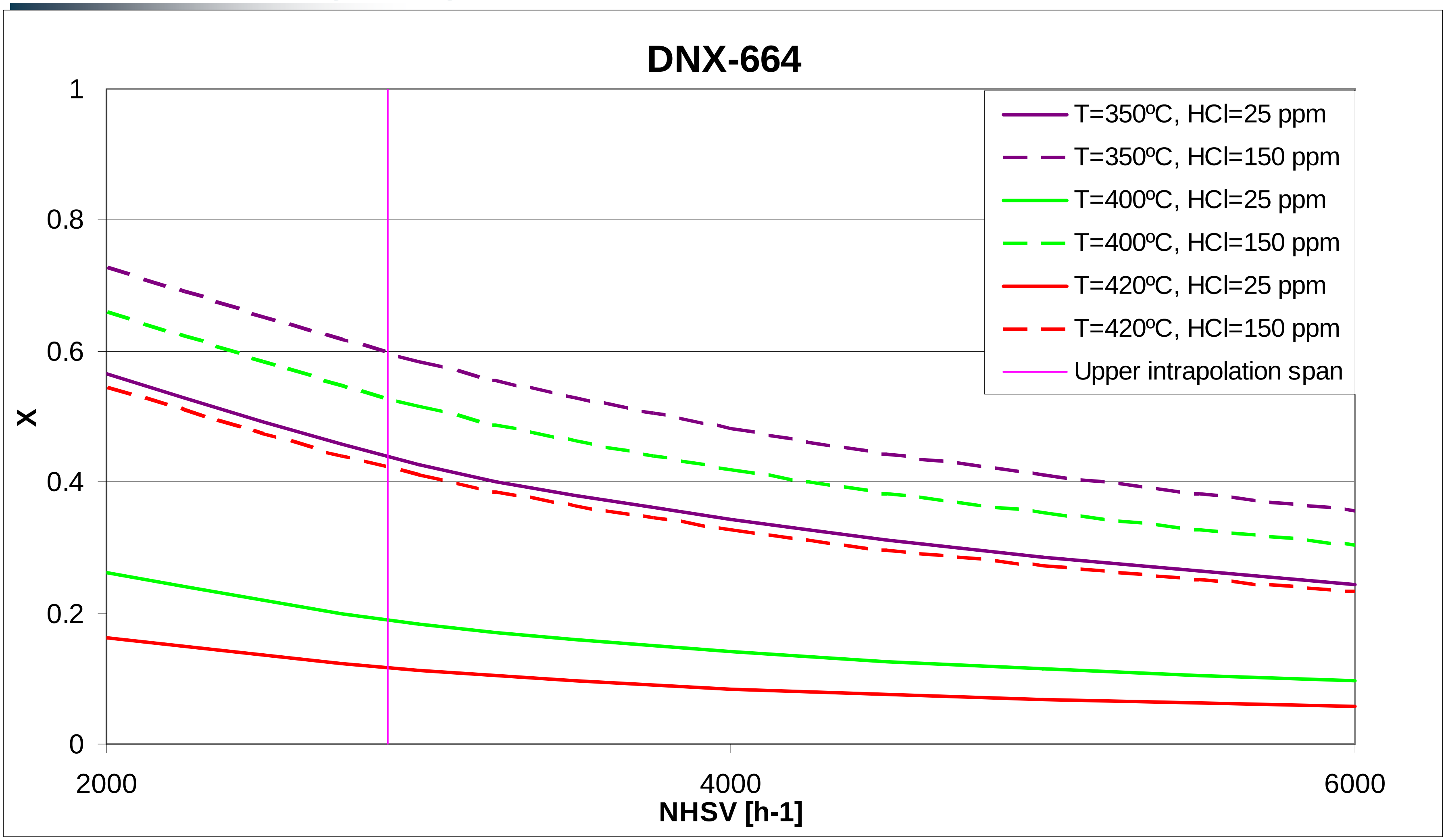
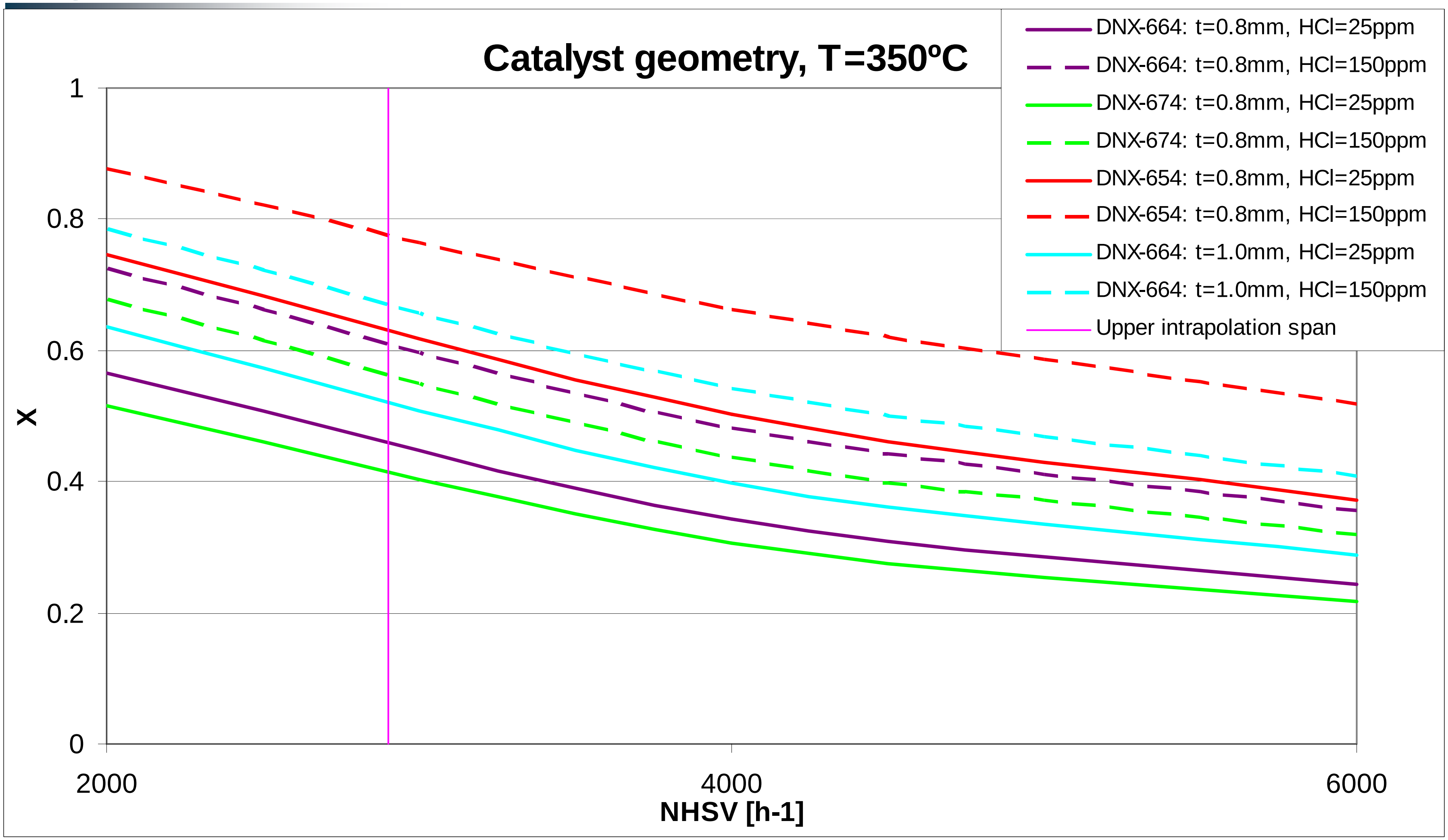
Modeling Hg^0 Oxidation across NHSV



Modeling Hg^0 Oxidation for different geometries



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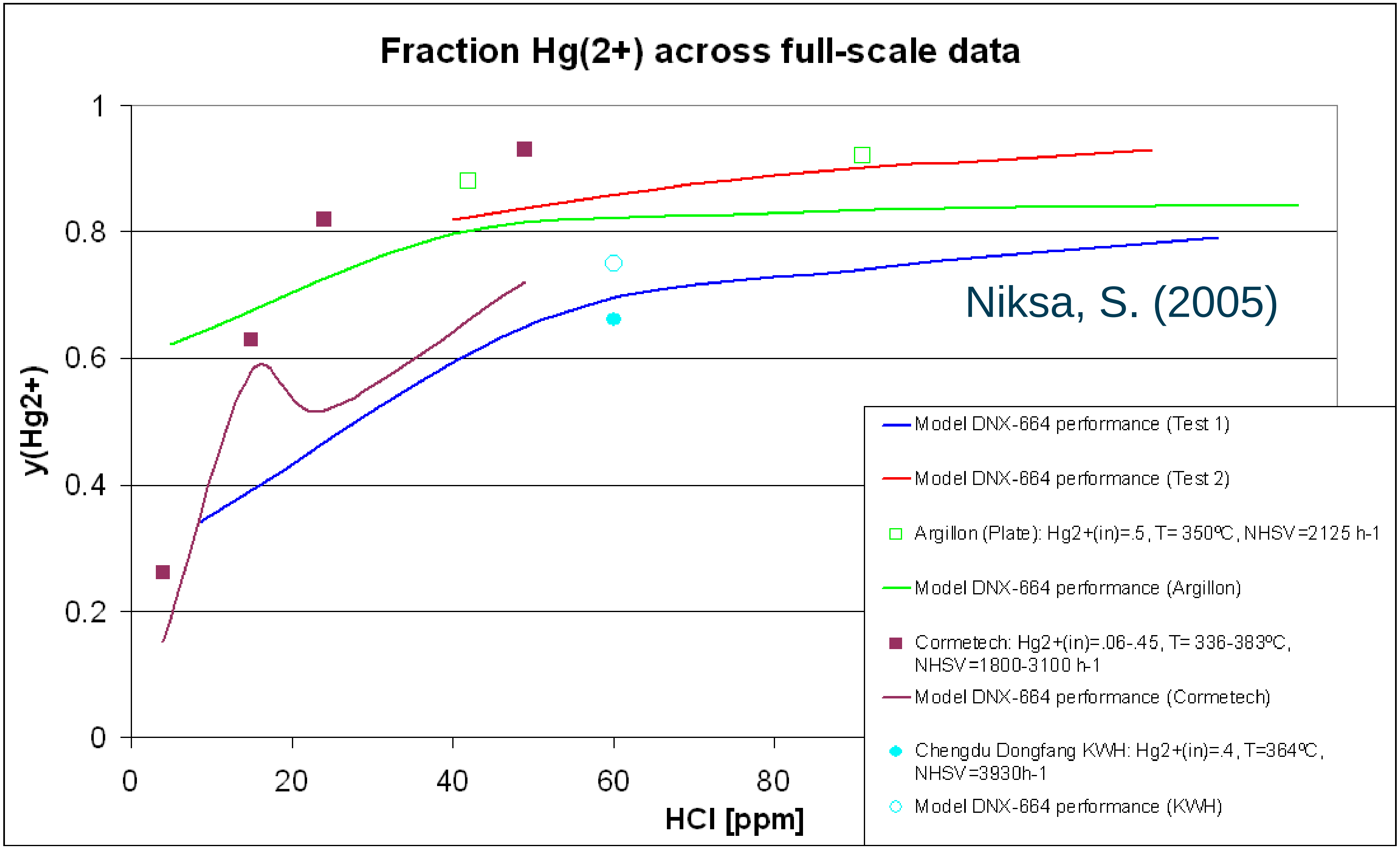
Performance of other catalyst

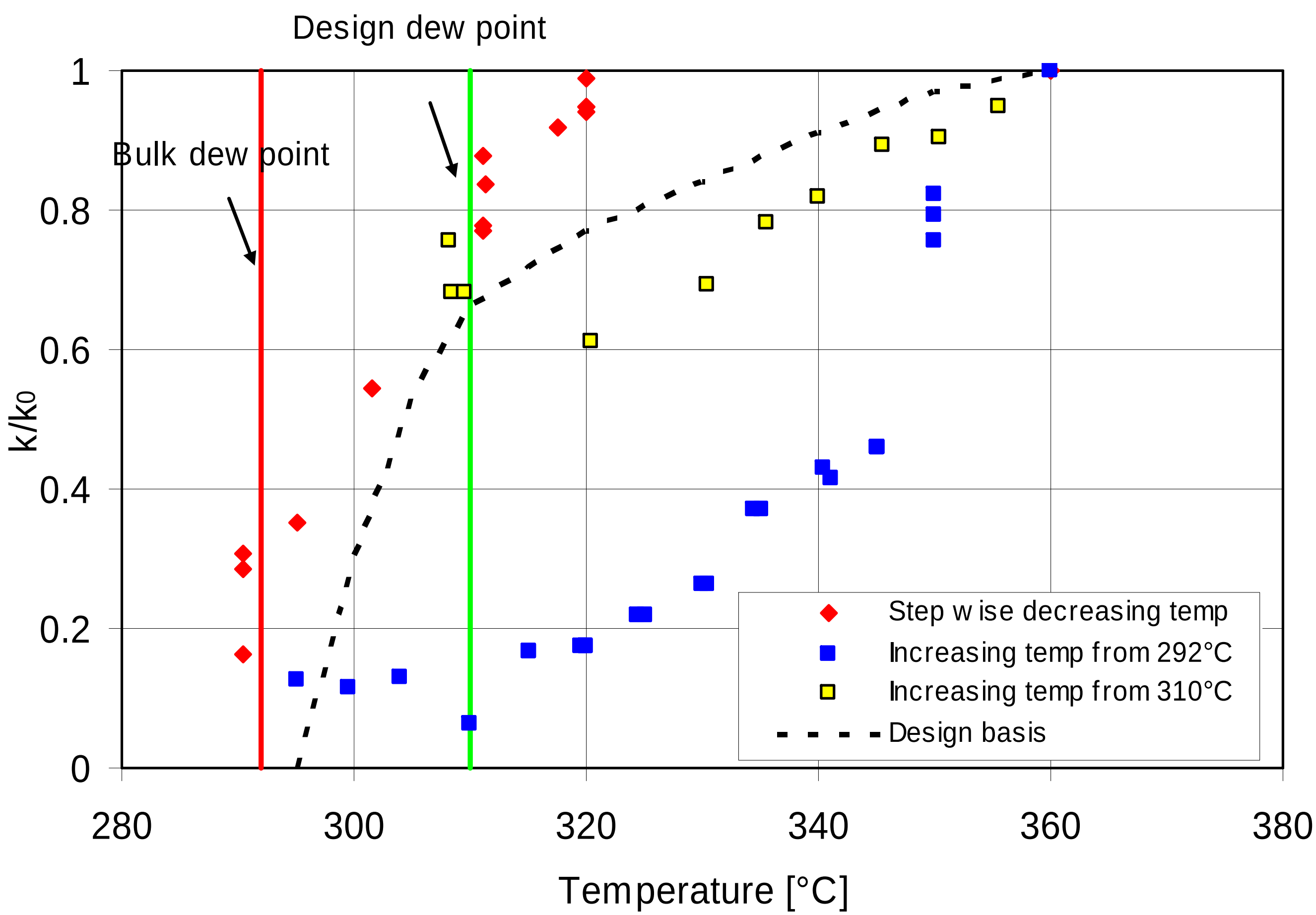


Conclusions

- Typical SCR-installations (T=350ºC, NHSV=3500 h-1) give ~ 50% conversion of Hg^0 for a high chlorine concentration
- Most favourable operating conditions (low temp, low flow) give up to 70% conversion.

Reduced load operation

- ABS inhibition at typical coal-fired conditions



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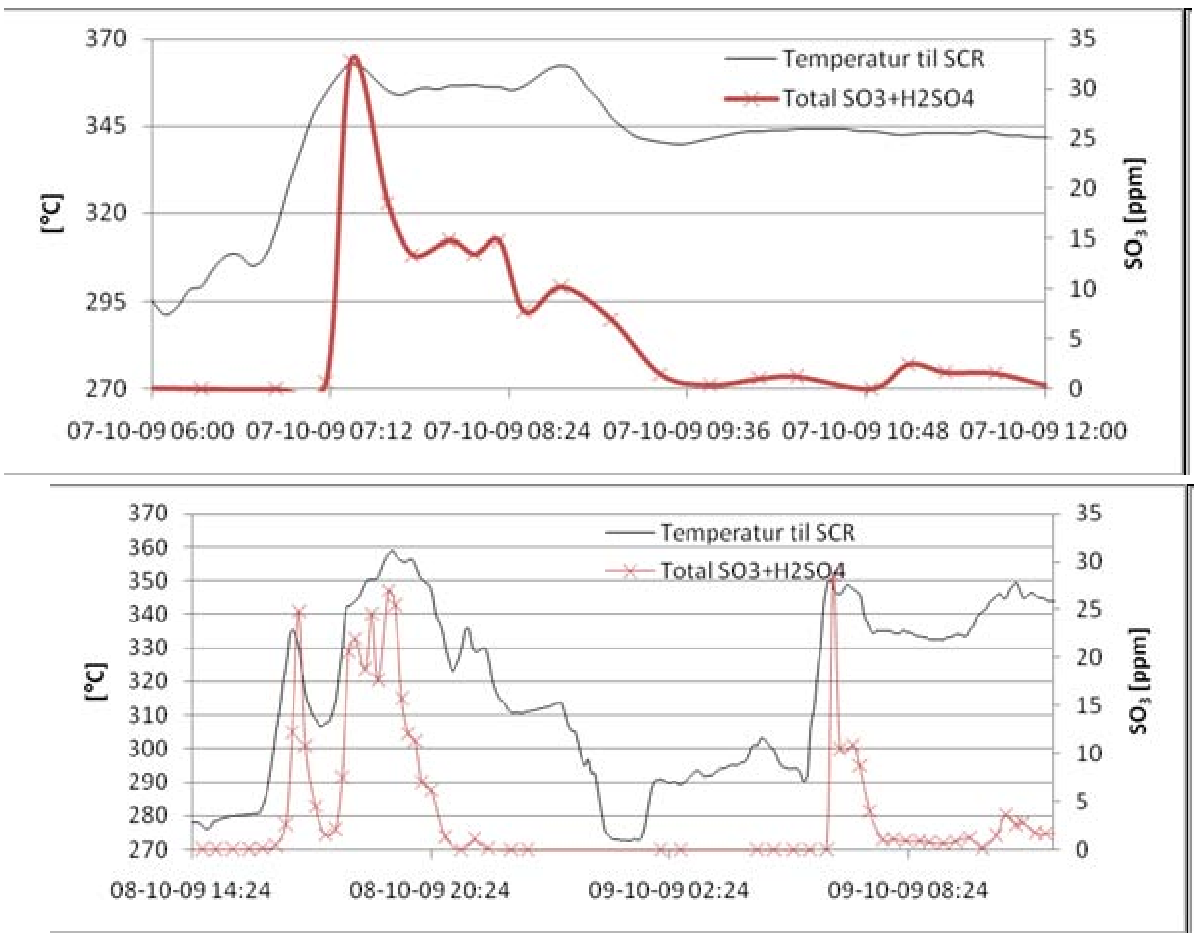
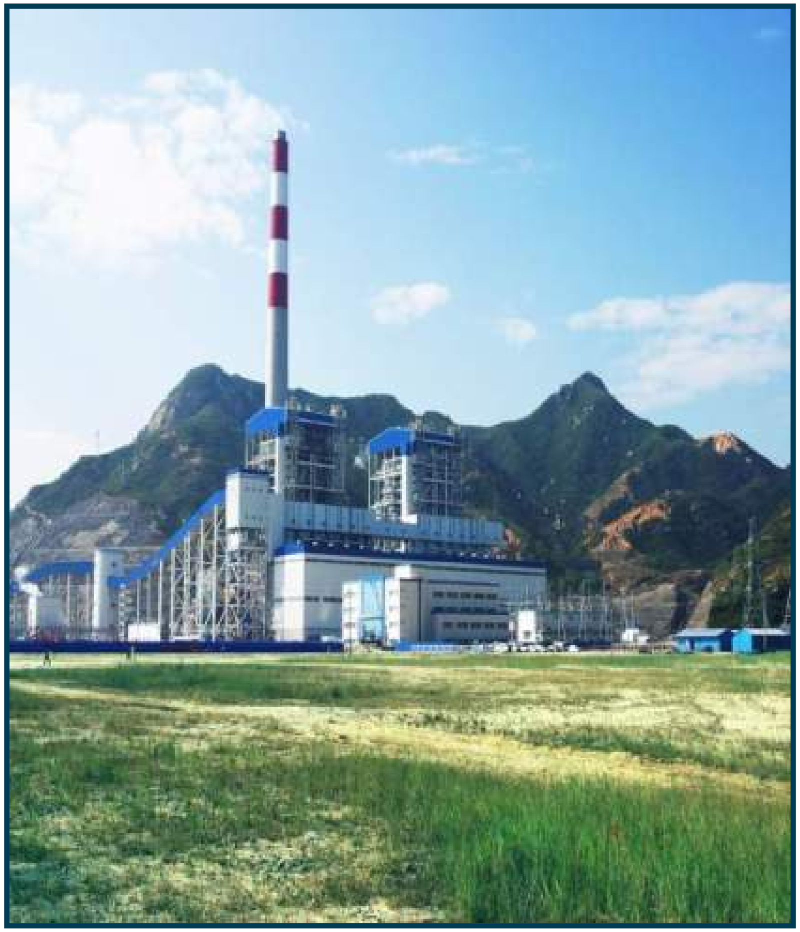
ABS formation/regeneration



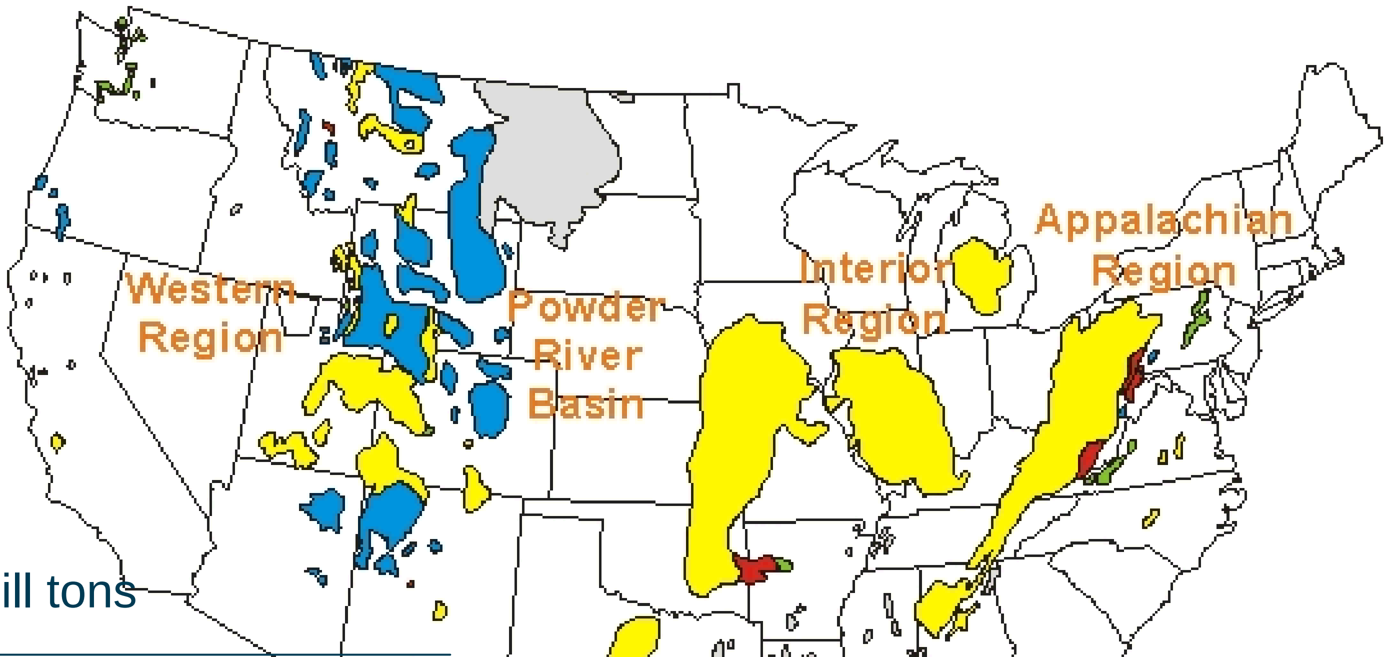
Ref: Dong Energy 2009

Tail End SCR

- 2 x 260 MWe, 2 x 300 MWe PC boilers, PRB fired
- Low Dust, Tail End SCR
- Vertical down flow
- NOx Inlet, 100 ppm
- NOx reduction, 57%
- SCR temperature 490°F
- Service Life – 32,000 Hours
- SCR inlet SO_3, < 1 ppm (calc. ABS dew point greater than operating temperature)
- Install Date - 2011



US coal production quality



2003 production mill tons

86

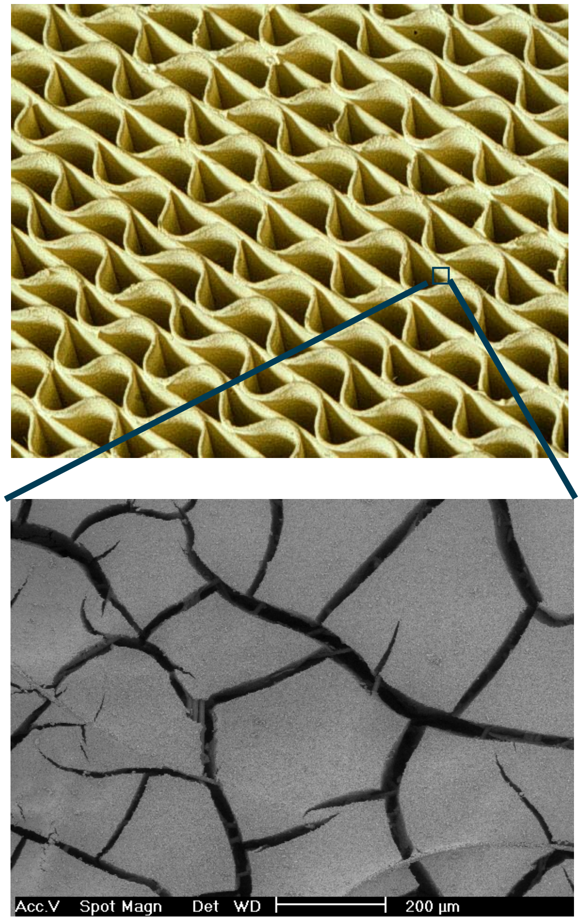
443

542 (50% high As)

1

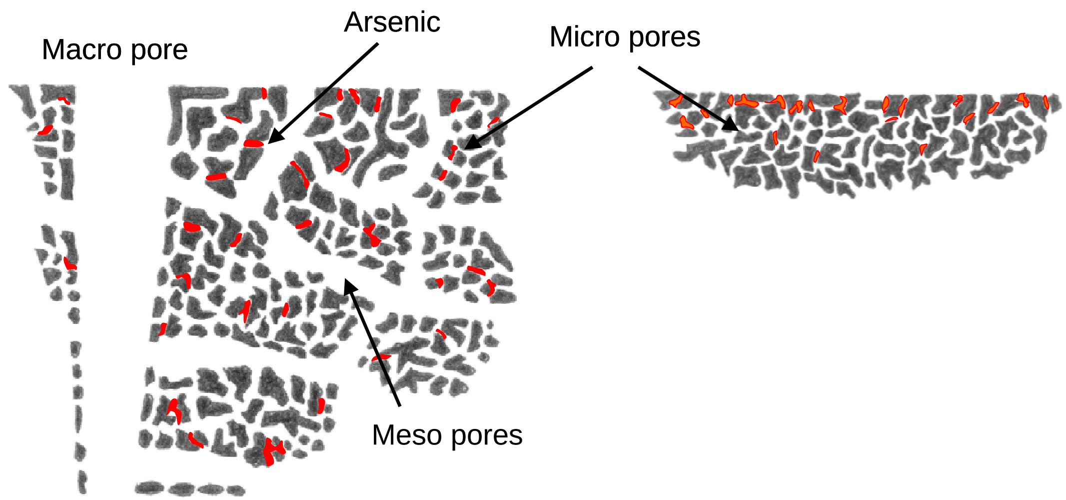
Source: Mcilvaine conpany

Presence of macroporosity: Resistance towards As-deactivation



Trimodal pore structure

Homogenous micro pore structure



As content in catalyst (ppm)

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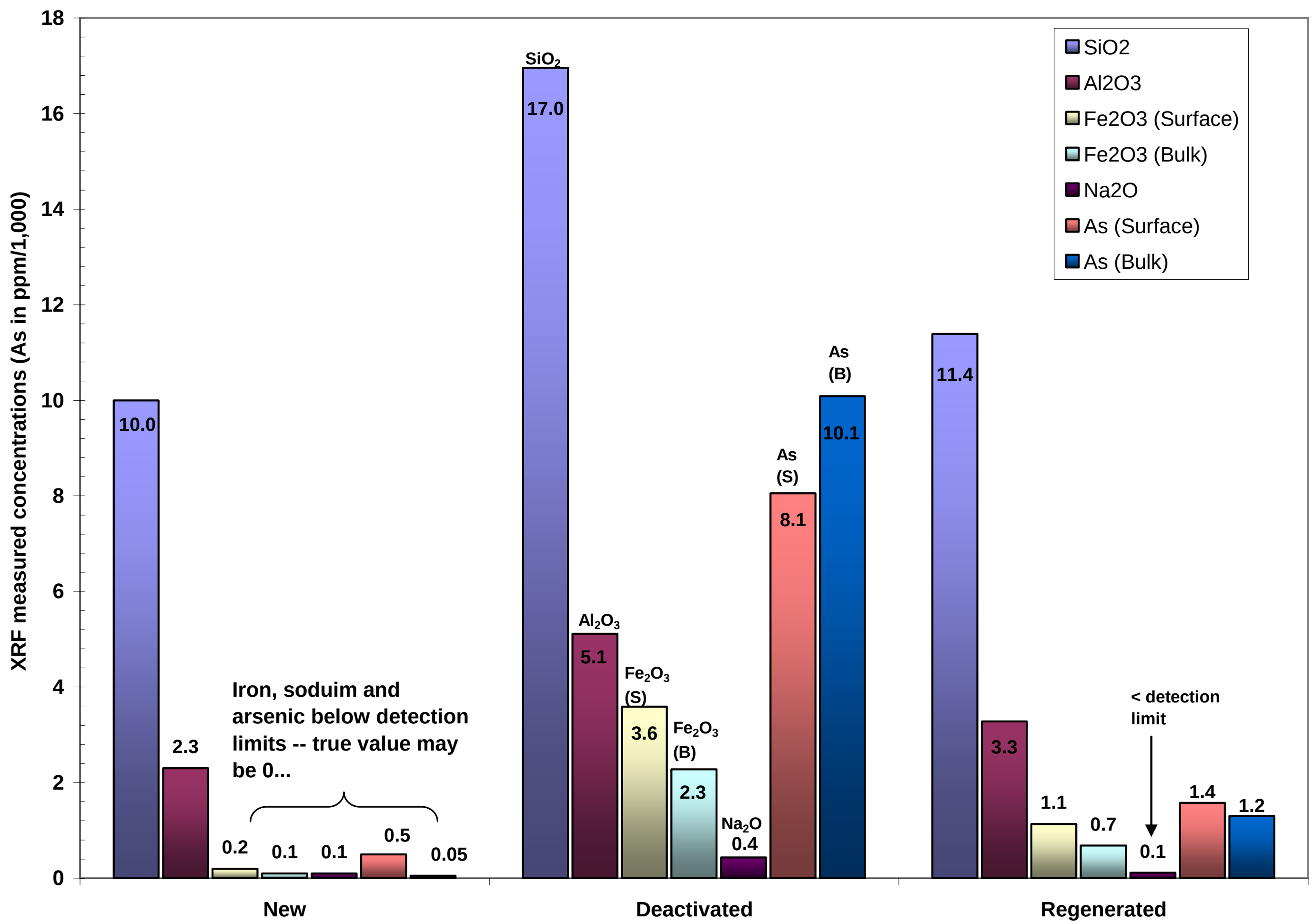
Catalyst regeneration

Source: SCR Tech, EPRI meeting 2008

Catalyst regeneration

- Mechanical cleaning
- Catalyst washing
- Catalyst re-impregnation

Removal of catalyst poisons



Source: SCR Tech, EPRI meeting 2008

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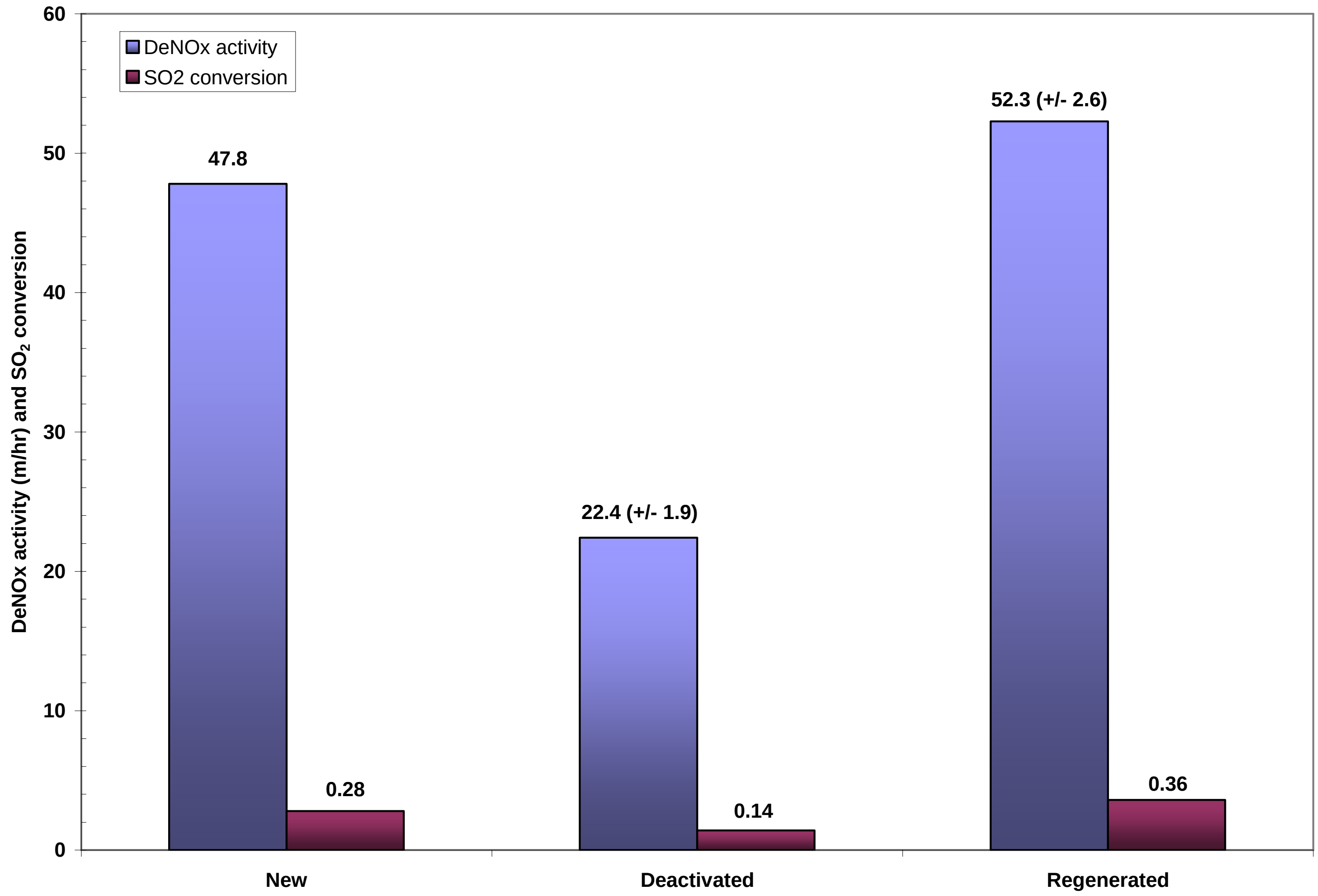
Activity of regenerated catalyst



Source: SCR Tech, EPRI meeting 2008

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Gas turbines

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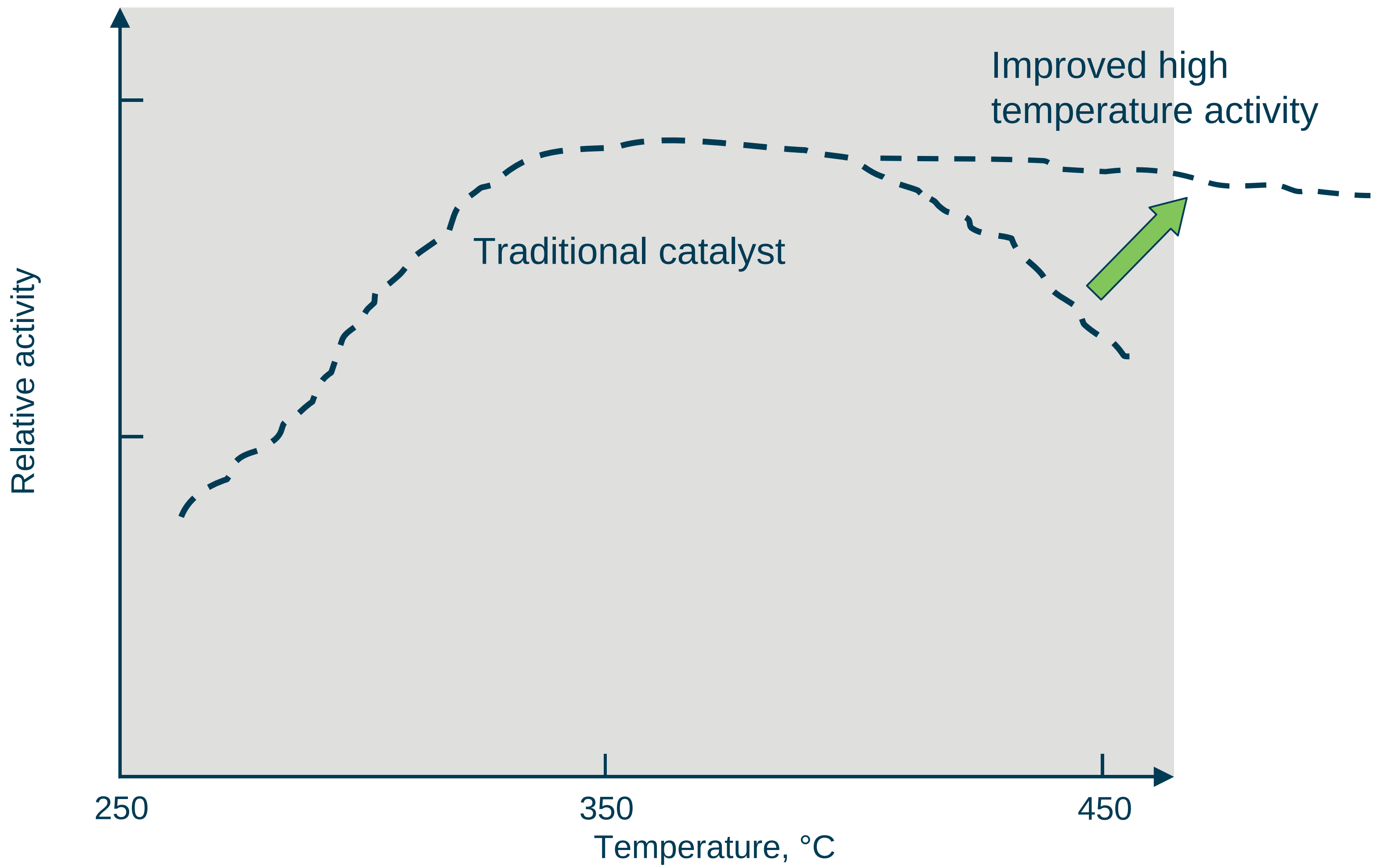
Gas turbines

- Peaker units/combined cycle retrofits
  - High temperature SCR (500 – 600°C)
  - Frequent start ups
  - Fast temperature ramps

Gas turbine catalyst



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SCR DeNOx on marine vessels

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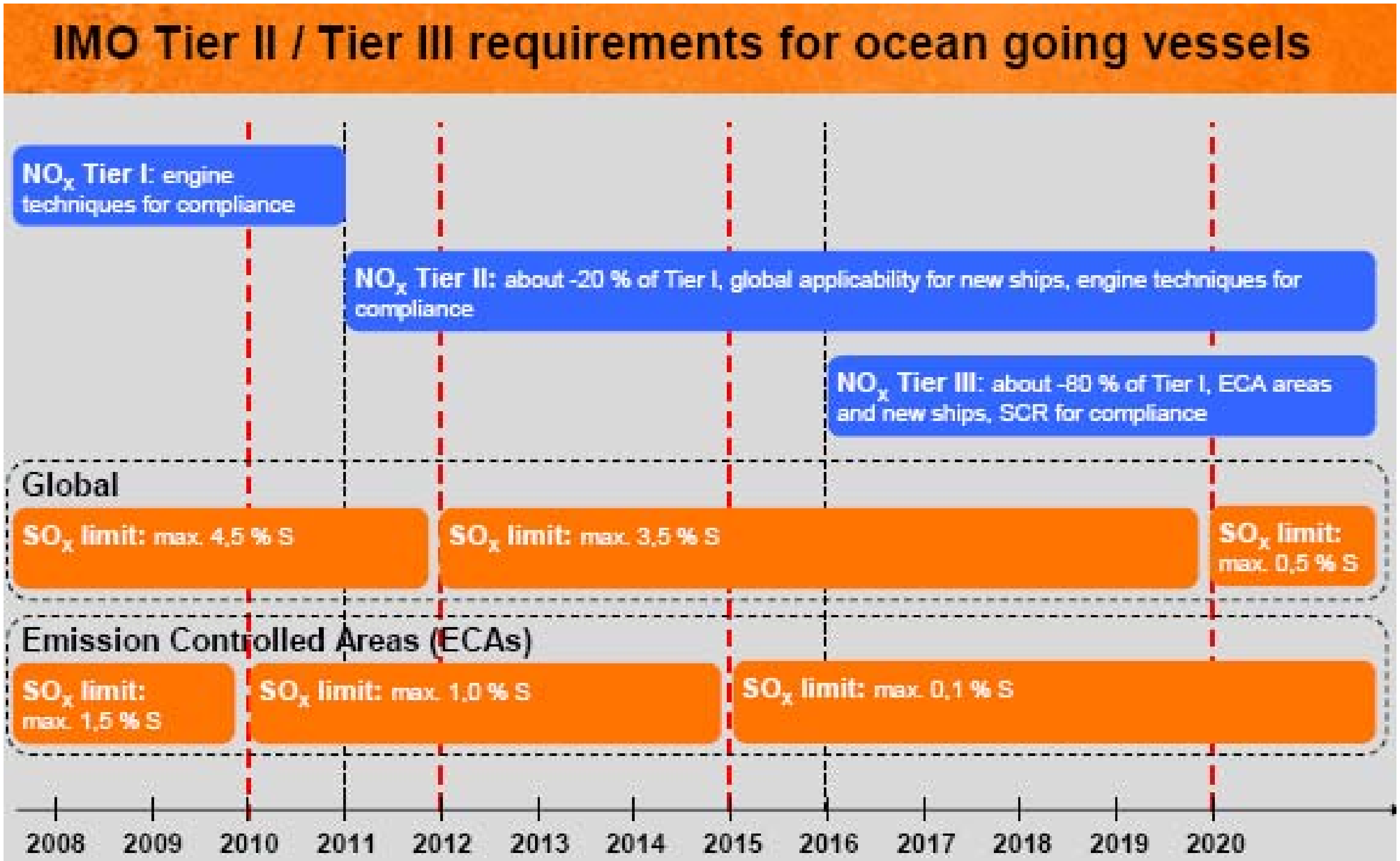
IMO requirements for marine vessels (Oct. 2008)



Source: Wärtsila CIMAC meeting 2008

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Emission compliance strategy

- Fuel type
  - Distillate fuel, low sulphur HFO or high sulphur HFO
- Emission control systems
  - SO_2 scrubbers
  - SCR DeNOx - Only possible with up to 1% S in fuel on 2-stroke engines with current technology
  - EGR

Nam Cheju
40 MW 2-stroke diesel

Source: MAN BW Gas October 2008

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Marine fuel prices

Latest Bunker Prices

	IFO380	IFO180	MDO	MGO
Singapore	432.50 ▲ +1.00	441.50 ▲ +3.50	545.00 ▼ -9.00	571.00 ▲ +3.50
Houston	404.00 ▲ +8.00	418.00 ▲ +11.00	549.00 ▲ +9.00	
Rotterdam	410.50 ▲ +8.00	429.00 ▲ +7.50	536.50 ▲ +10.50	582.50 ▲ +11.00
Fujairah	435.00 ▲ +3.50	463.00 ▲ +8.50		625.00 ▲ +4.50

Source: MAN August 2009

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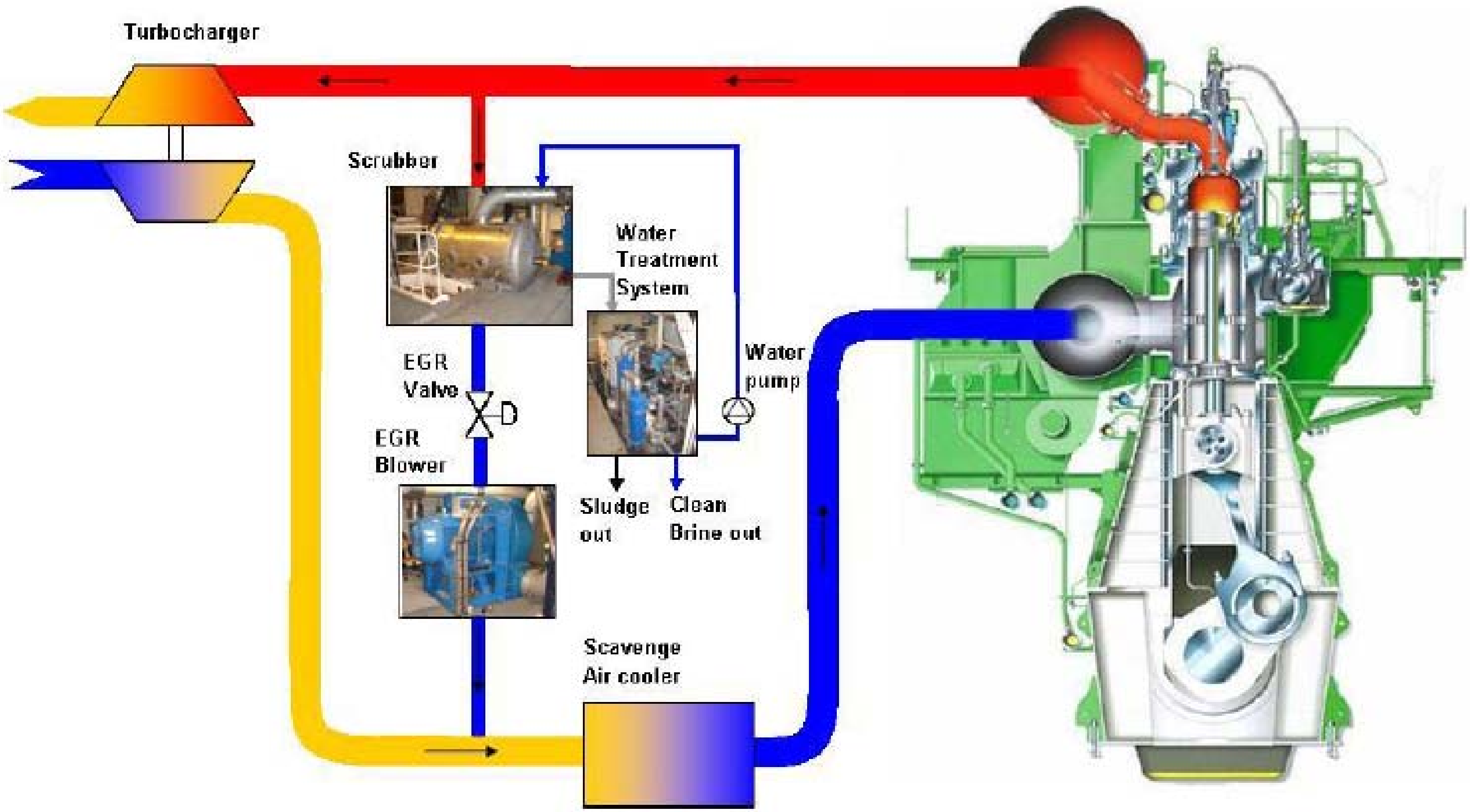
EGR


Turbocharger
Scrubber
Water
Treatment
System
Water
pump
EGR
Valve
EGR
Blower
Sludge
out
Clean
Brine out
Scavenge
Air cooler

New catalyst developments

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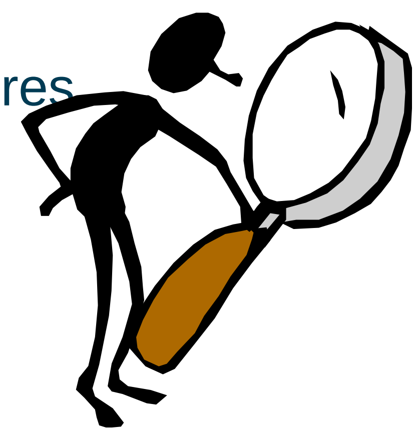
Haldor Topsoe SCR catalyst developments

- Biomass optimized catalysts
  - Competitive sites for poison binding
  - Catalyst system with inhibition of poison diffusion
  - Higher intrinsic activity through increased number of active sites
- Low temperature catalysts
  - More active sites
  - Improved design basis
- Gas turbine peaker unit catalysts
  - Improved activity and durability at high temperatures
- New SCR DeNOx technologies
  - Cerafil TopKat™



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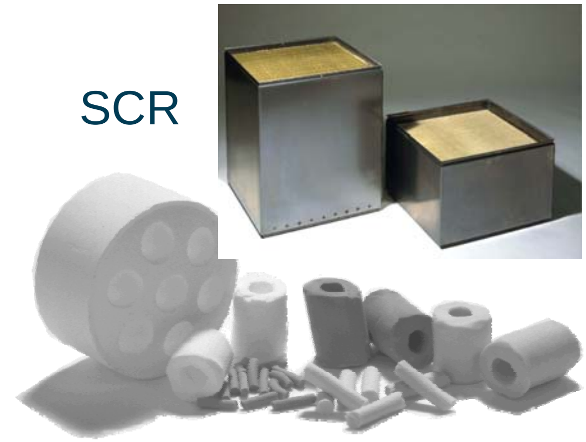
Catalytic filter technology: Cerafil TopKat

The combination of two well established and effective technologies

Cerafil XS + SCR



CLEAR EDGE Filtration

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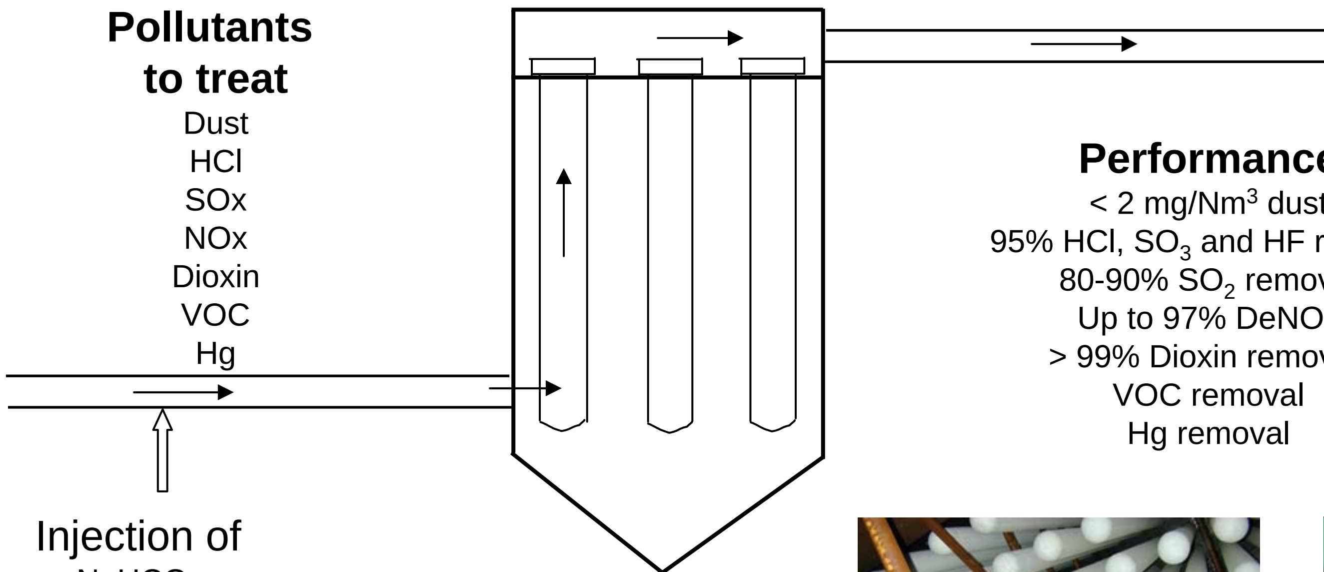
Cerafil ® TopKat
multi pollutant control device

Temperature window 350-700°F

Pollutants to treat

Dust
HCl
SOx
NOx
Dioxin
VOC
Hg



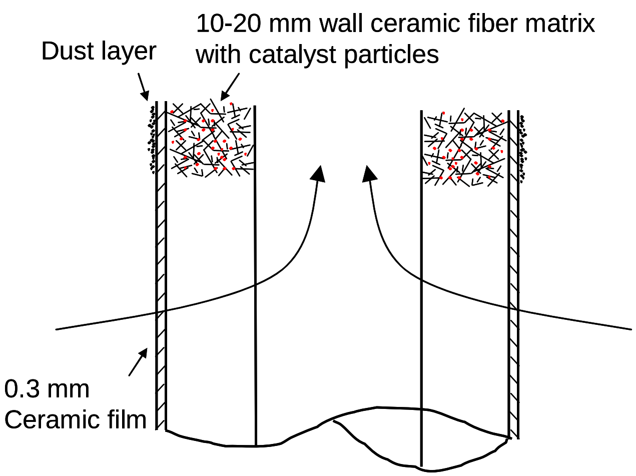
Injection of
$NaHCO_3$
CaO
NH_3
Mercury sorbent
Support air

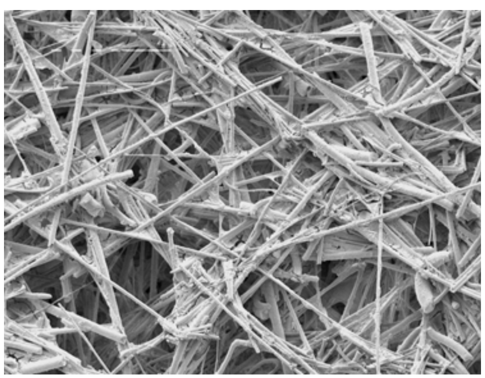
Performance

< 2 mg/Nm^3 dust
95% HCl, SO_3 and HF removal
80-90% SO_2 removal
Up to 97% DeNOx
> 99% Dioxin removal
VOC removal
Hg removal

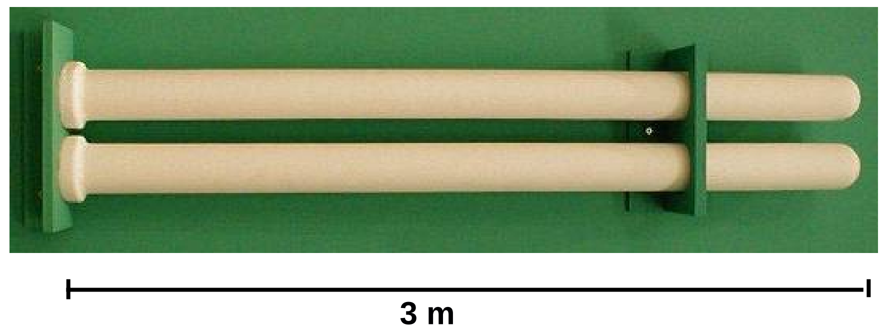
Catalytic activated dust filters

- Ceramic fiber matrix impregnated with catalyst

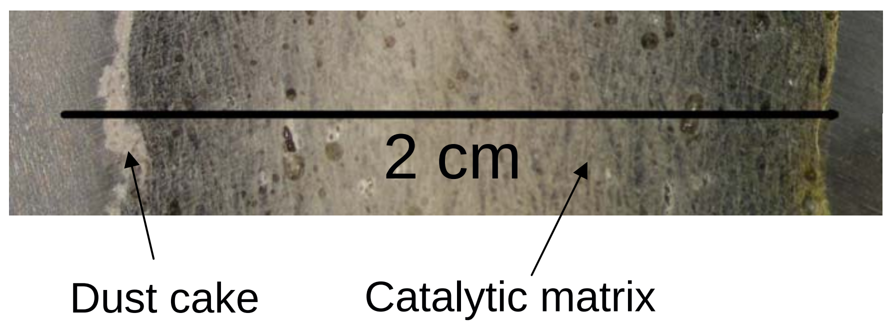




CTK - 3000



Wall cross section



Cerafil ® TopKat benefits

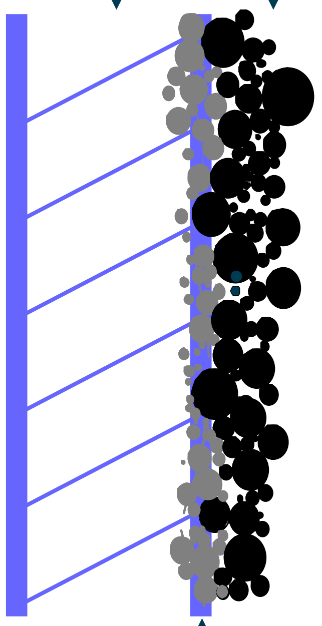
- High ash removal efficiency: < 2 mg/Nm3 slip
  - Comply with strict emissions legislation
  - Stable long term operation

- Temperature resistant to 700°F
  - Avoid bag burning problems
  - Potential for heat recovery from clean gas
  - Effective acid gas scrubbing
  - Maintain optimal temperature for SCR DeNOx
  - Max temperature determined by the stability of the vanadia/titania system
  - The un-impregnated Cerafil filter is temperature resistant up to 1650°F
  - Temperature excursions up to 790°F is allowed

- Corrosion resistant
  - Stable inert oxide structure
  - Resistant to condensing acid

Filtration mechanism

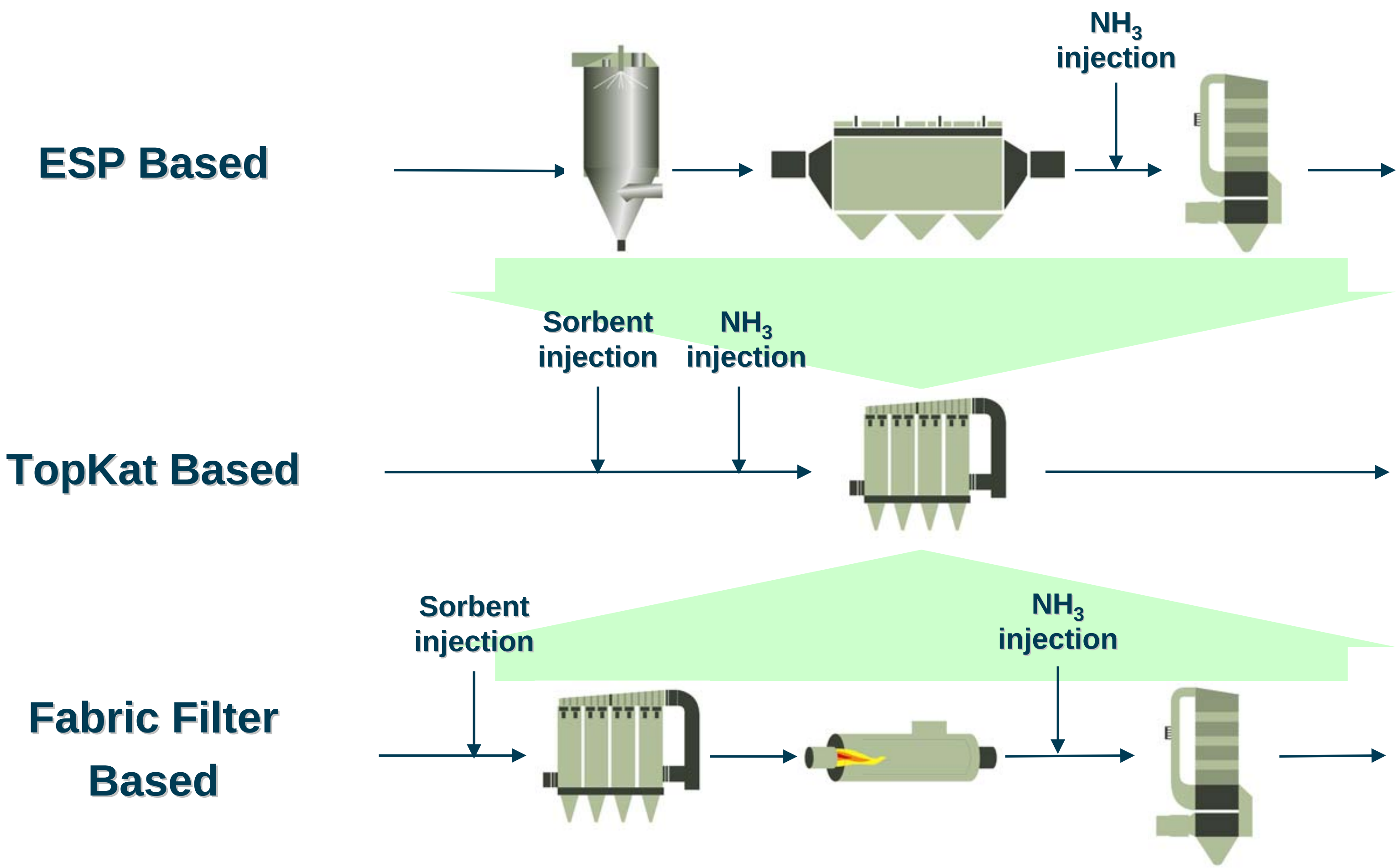
- Pre-conditioning with an inert powder
- Development of residual layer
- The dust cake builds up on top of the residual layer
- The cake is periodically removed with a reverse pulse of air



The filtration mechanism provides

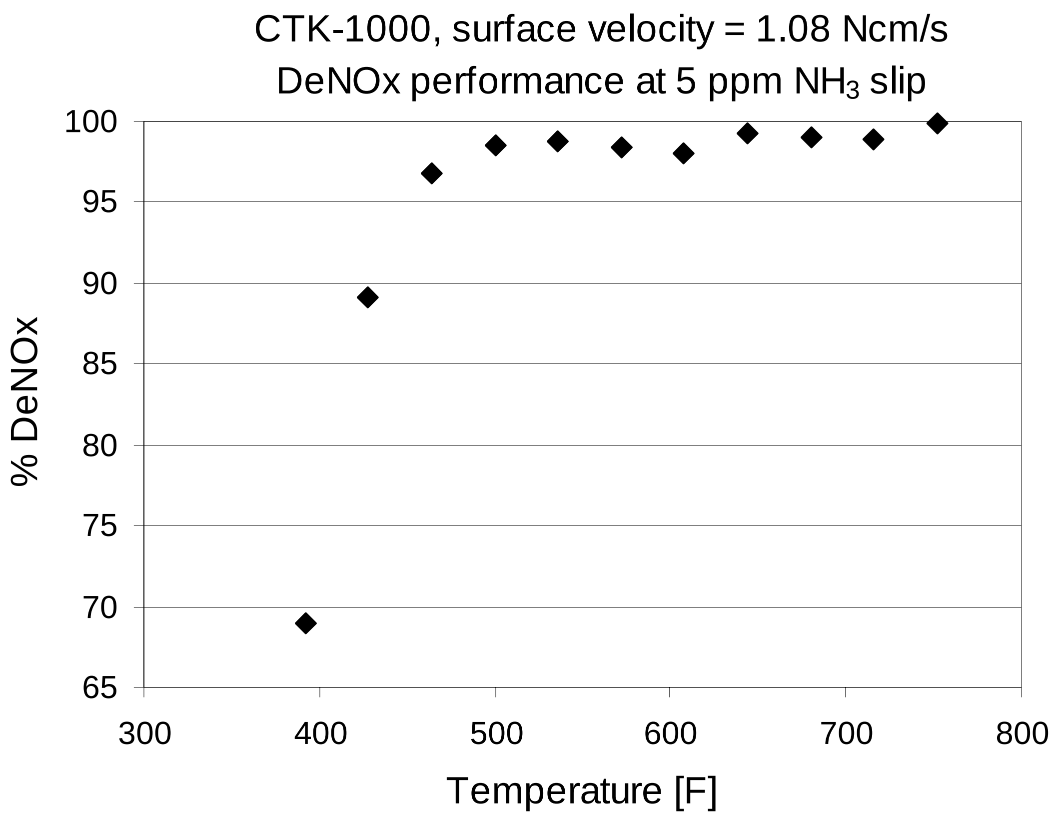
- High efficiency
- Negligible depth penetration which protects catalyst from poisoning
- Potential for long life

Equipment train options for dust, SOx & NOx

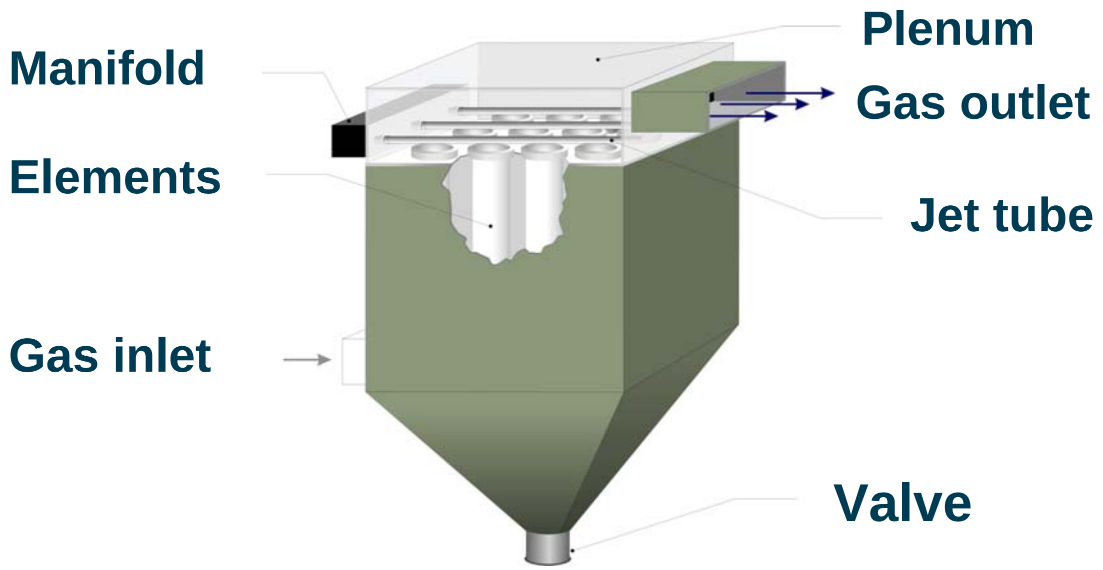


DeNOx performance

$4\ NO + 4\ NH_3 + O_2 \Rightarrow 2\ N_2 + 6\ H_2O$

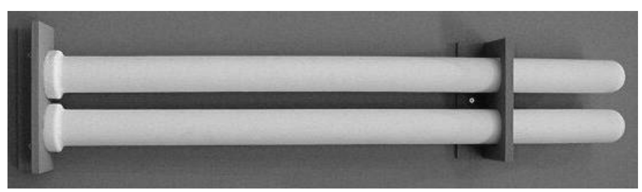


Filter plant layout



TopKat Reference List

Duty	Year	Location	Quantity	Element type	Filtration temp [°F]	DeNOx [%]	Dioxin inlet [ng/Nm3]	Dioxin outlet [ng/Nm3]	Comment
Clinical waste incineration	2004	UK	270	CTK-1000	311		75	0.55	
Meat processing waste incineration	2006	France	80	CTK-3000	392-473			0.011	
Glass furnace	2006	Belgium	40	CTK-3000	662	83			Pilot
Meat processing waste incineration	2007	France	40	CTK-3000	428	93			Pilot
Meat processing waste incineration	2008	France	672	CTK-3000	536	85			
Wood waste incineration	2008	Japan	540	CTK-3000	518		33	1	
Animal carcass incineration	2008	Japan	540	CTK-3000	437		16	0.008	
Animal carcass incineration	2009	UK	64	CTK-3000	356			0.0076	
Glass furnace	2009	Spain	1820	CTK-3000	662	80			



HALDOR TOPSØE

Applications in air pollution control

- Waste incineration
- Glass furnaces
- Sinter plants
- Large diesel engines
- Biomass fired boilers
- Coal fired plants with difficult ash
- Cement plants

TopKat in Glass Furnaces

Benefits

- Compact design (two/tree times more compact compared to Particulate/NOx control combinations)
- Improved heat recovery by limited fouling in the downstream heat recovery boiler
- < 2 mg/Nm^3 particulate slip
- SCR catalyst protected from poisonous sodium aerosols
- Possibility for phased implementation
- Favorable economy compared to other technologies

Mentioned as emerging technology in the European union BREF for the glass industry (draft July 2009)

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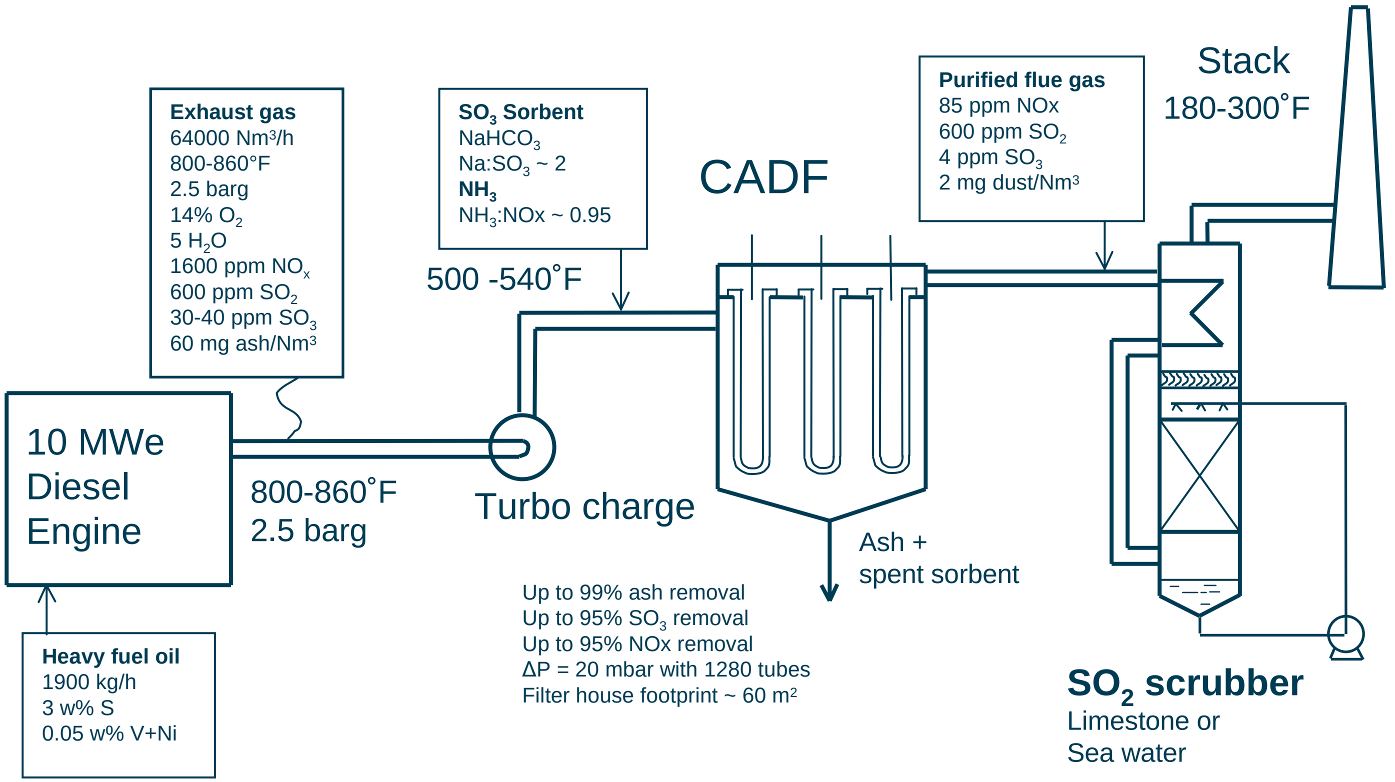
Topcat in HFO fired diesel engines



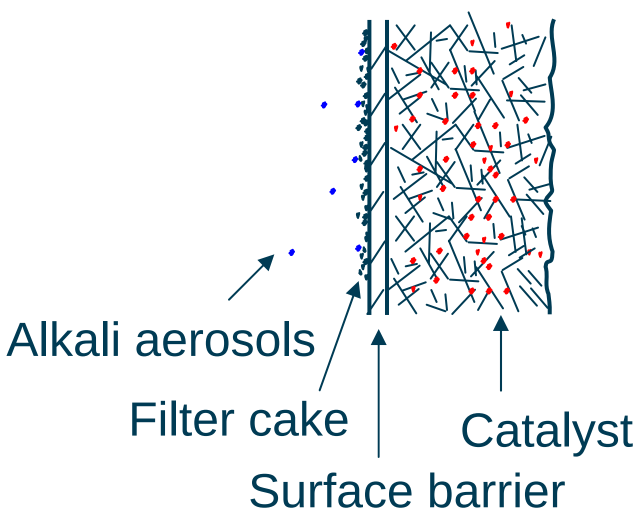
$$SO_3 + NH_3 + H_2O \rightarrow NH_4HSO_{4(l)}$$ FAST

$$4NaHCO_{3(S)} + 2NH_4HSO_{4(l)} + \tfrac{3}{2}O_2 \rightarrow 2Na_2SO_{4(S)} + (NH_4)_2SO_{4(S)} + 4CO_2 + 3H_2O$$ FAST

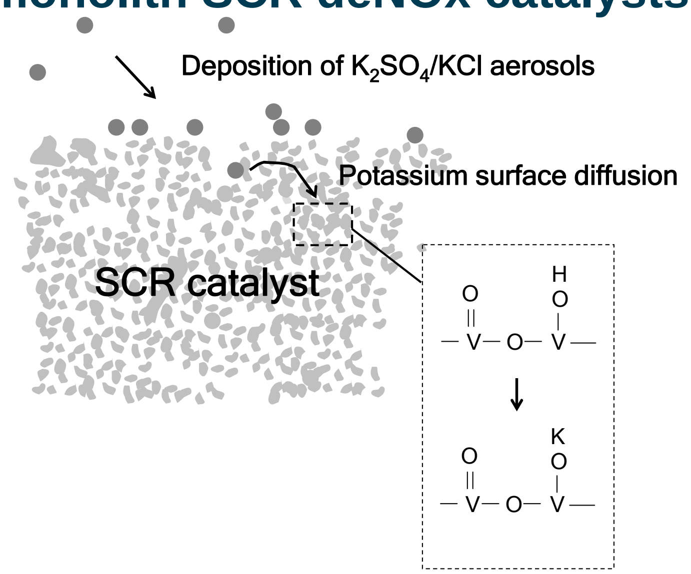
$$2NaHCO_{3(S)} + (NH_4)_2SO_{4(S)} + 2O_2 \rightarrow 2Na_2SO_{4(S)} + 2NH_3 + 2CO_2 + 4H_2O$$ SLOW: 90% conv during 1 hour at 480°F

Biomass fired boilers

- Catalyst is protected against the catalyst poisons sodium and potassium
- Catalyst life is extended



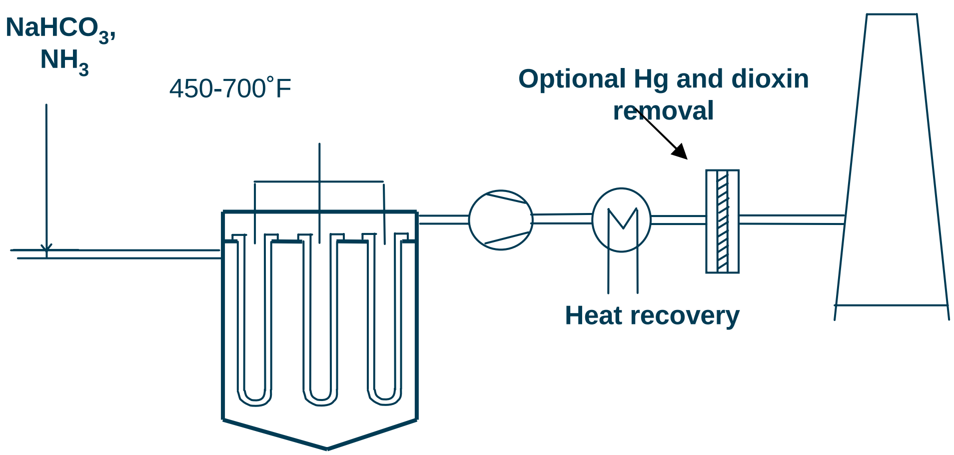
Alkali poisoning mechanism in monolith SCR deNOx catalysts



Waste incineration

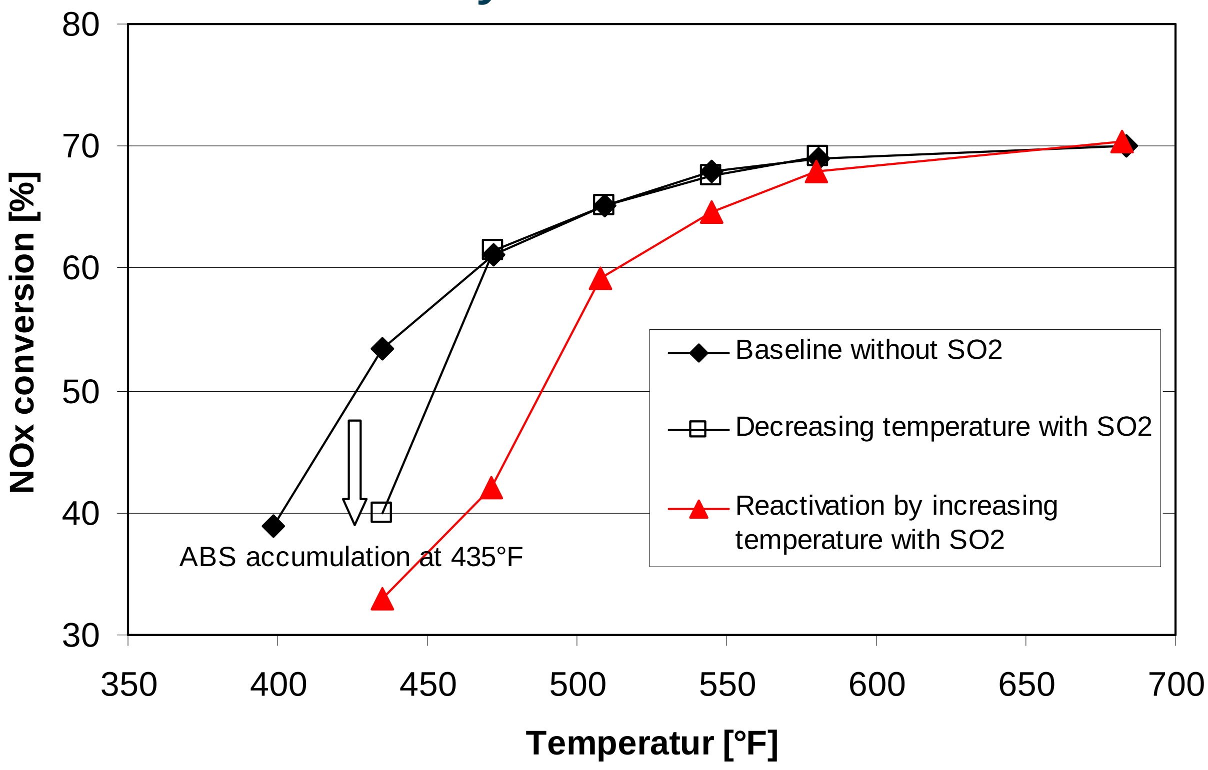
NO_x, SO_x, dust and dioxin emission control

- **Design issues**
- DeNovo Dioxin formation
  - Temperature range 570-750°F
  - Catalyzed by Cu, Fe + heavy metals in dust
  - Suppressed by CaO, S, … NH3
- SO2 oxidation
  - 1.5% conversion at 570°F
  - Catalyzed by V2O5
- Minimum temperature
  - ABS dew point NH3(g) + H2SO4(g) → NH4HSO4(l)
  - Sub dew point operation possible with sorbent injection. Reheat option required
  - Even though SO3 is effectively removed there is still a minimum temperature due to formation of SO3 in the catalyst itself



Effect of SO2 on DeNOx activity

- Inhibition of pure SO2 below 450°F due to ABS formation inside catalyst

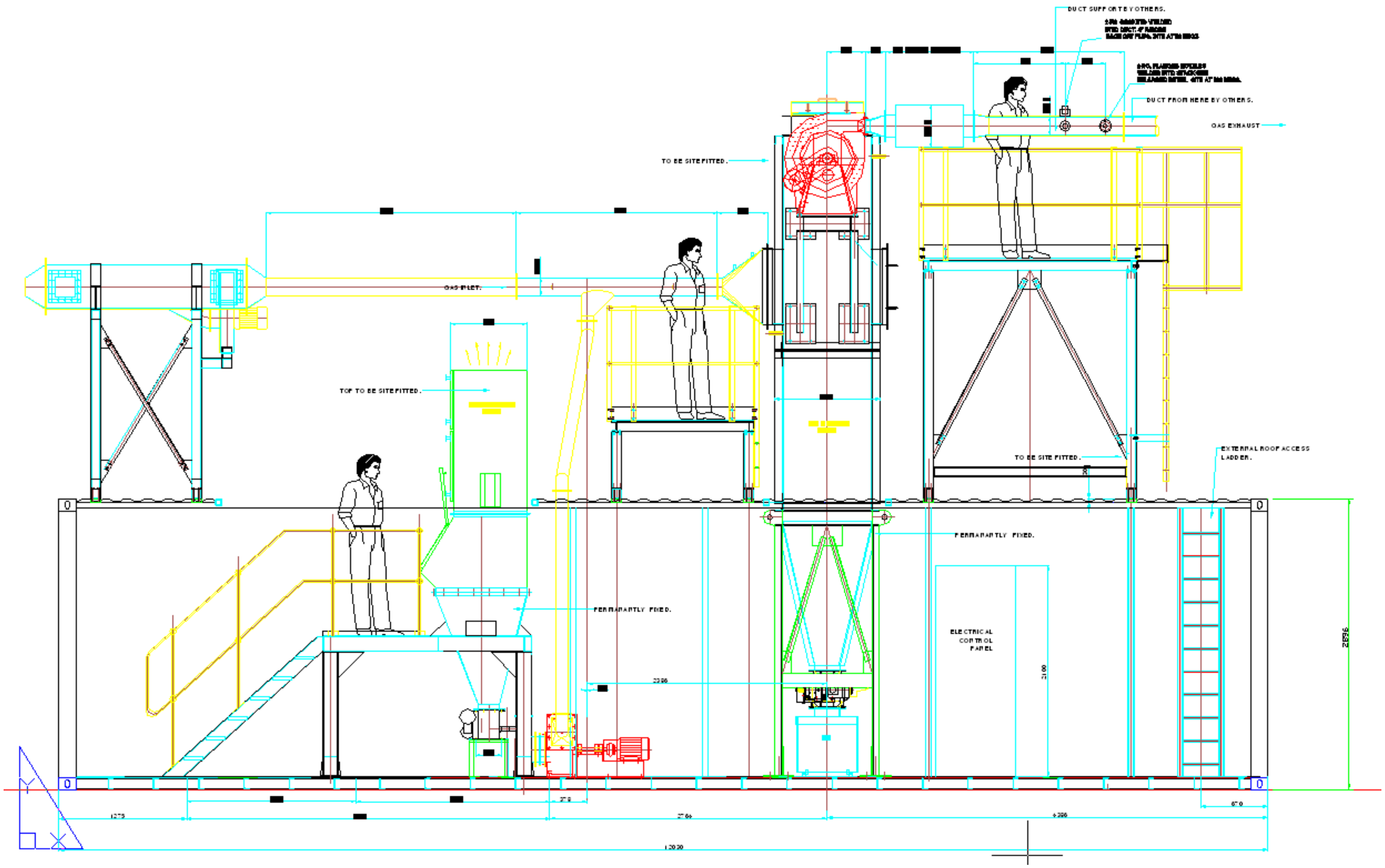


HALDOR TOPSØE

Cerafil ® TopKat Plant Dimensions

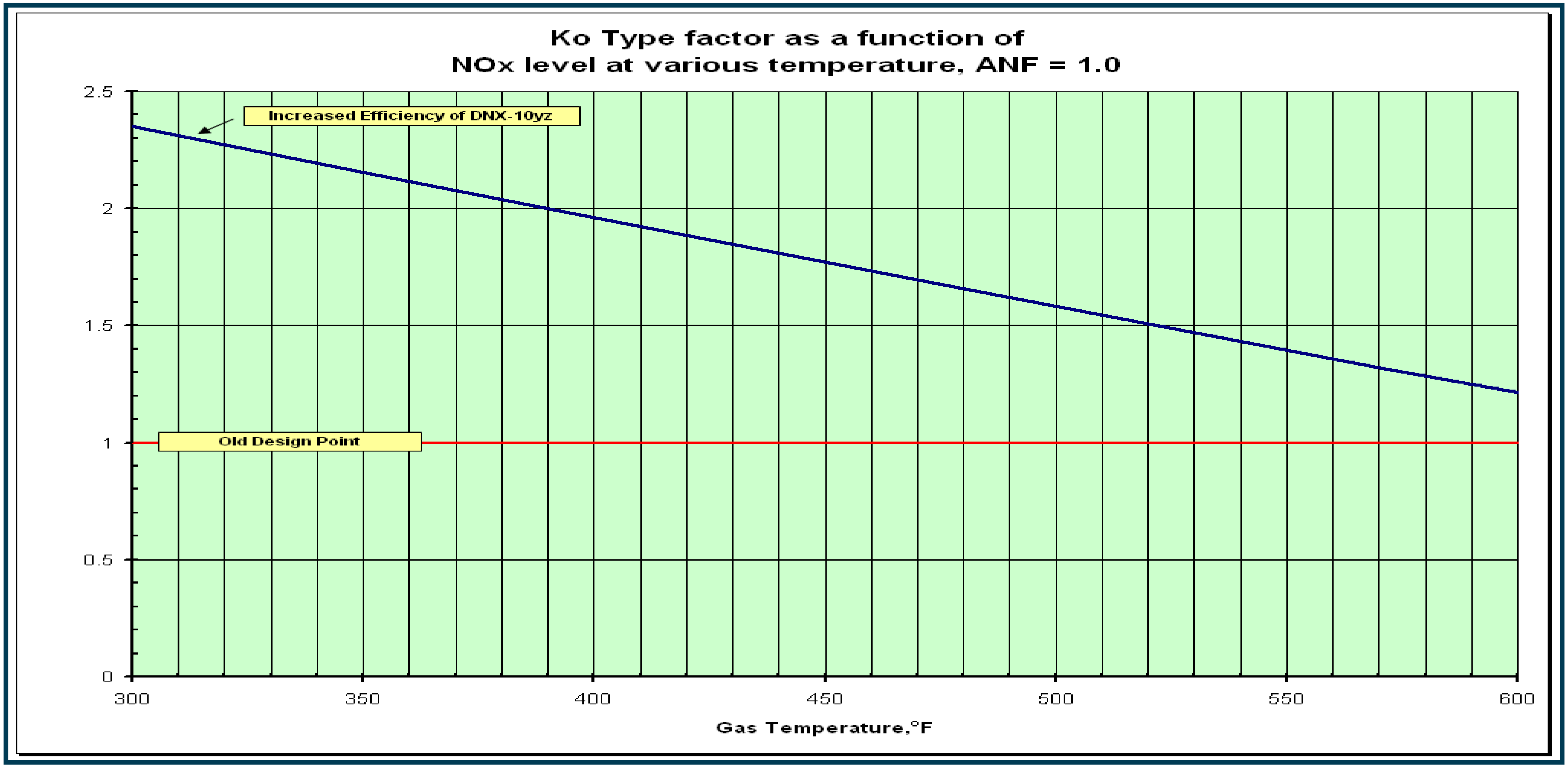
- 100,000 Nm^3/h
- Fuel = biomass (wood)
- 2800 candles
- Target pressure drop
  $\Delta P \approx$ 150 mm H_2O (1.5 kPa, 5.9" WC)
  (Maximum pressure drop)
- Clean dust free candle
  $\Delta P \approx$ 30-40 mm H_2O
- Cleaning cycle 600-3600 seconds
- Pressurized air consumption
  15 liters/candles/pulse
- Filter house footprint = 130 m^2

Pilot Layout



Lower Temperature SCR Operation

Improved activity at lower temperature



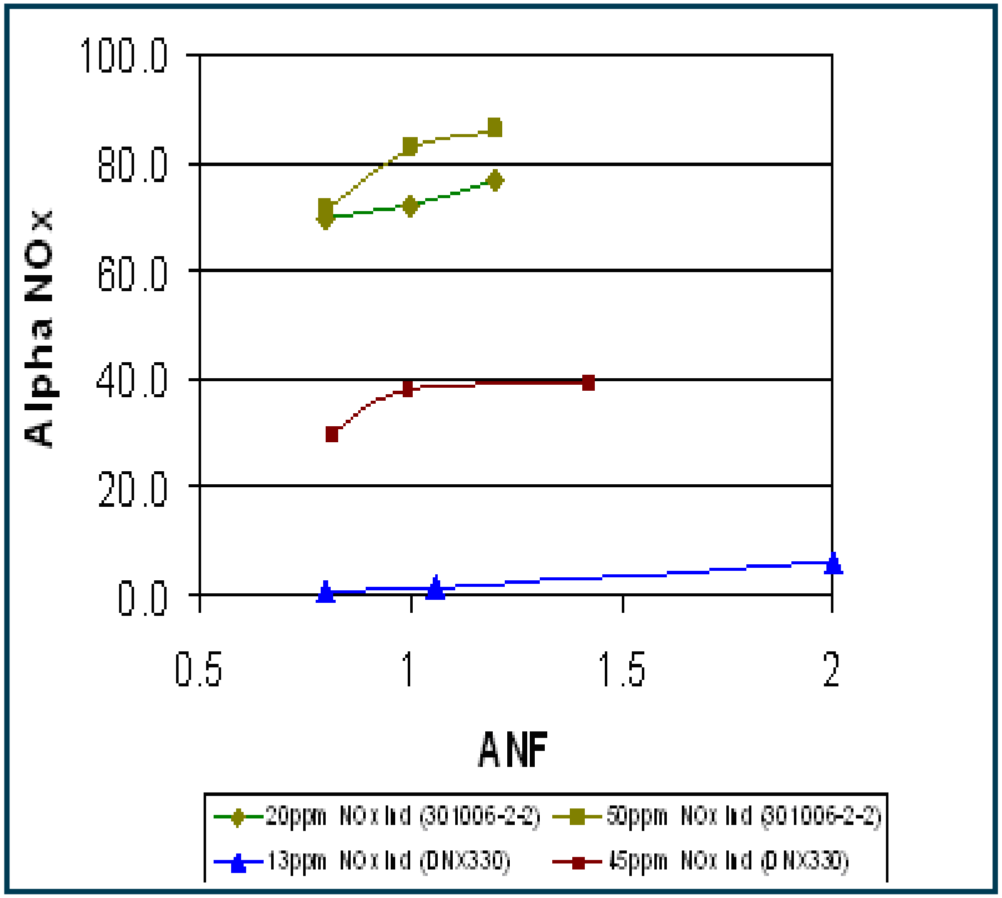
HALDOR TOPSØE

Synerprise Project - Site 16 MW CHP

- Grate fired boiler
- Fuel: Wood chips
- SCR installed in 2008
- Low dust, vertical up & down flow
- NOx Inlet, 0.18 lbs/mmBtu
- NOx reduction, 64%
- SCR temperature 340 - 360°F
- On line catalyst cleaning
  - reverse flow
- Catalyst deactivation is less than expected
- SCR inlet SO_3 < 0.5 ppm (calc. ABS dew point > 450°F

High Temperature SCR Operation

Improved activity at higher temperature

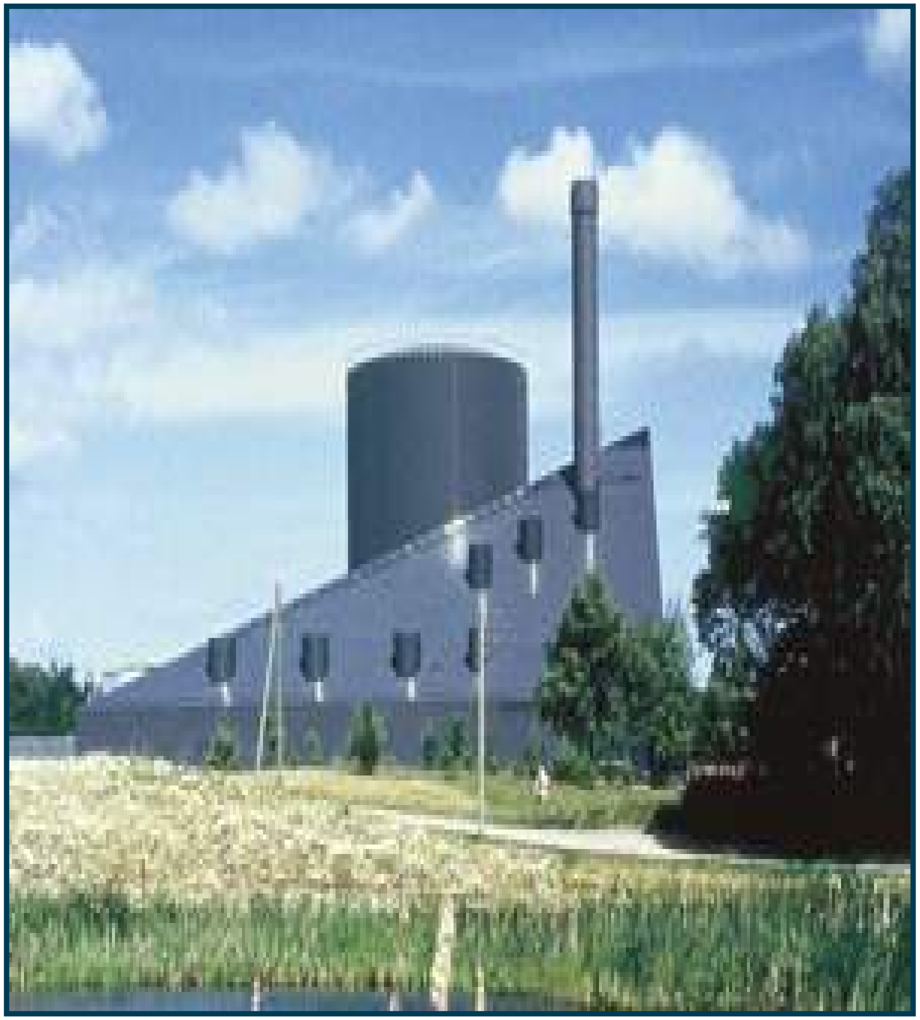


- DNX-029HiTe
  - Stronger NH_3 absorption
  - Lower NH_3 oxidation rate
  - Higher DeNOx activity

Simple Cycle Gas Turbines

- High temperature SCR (900 – 1,030°F)
- Frequent start ups
- Fast temperature ramps

New DNX-029HiTe Catalyst



Vra Power Plant

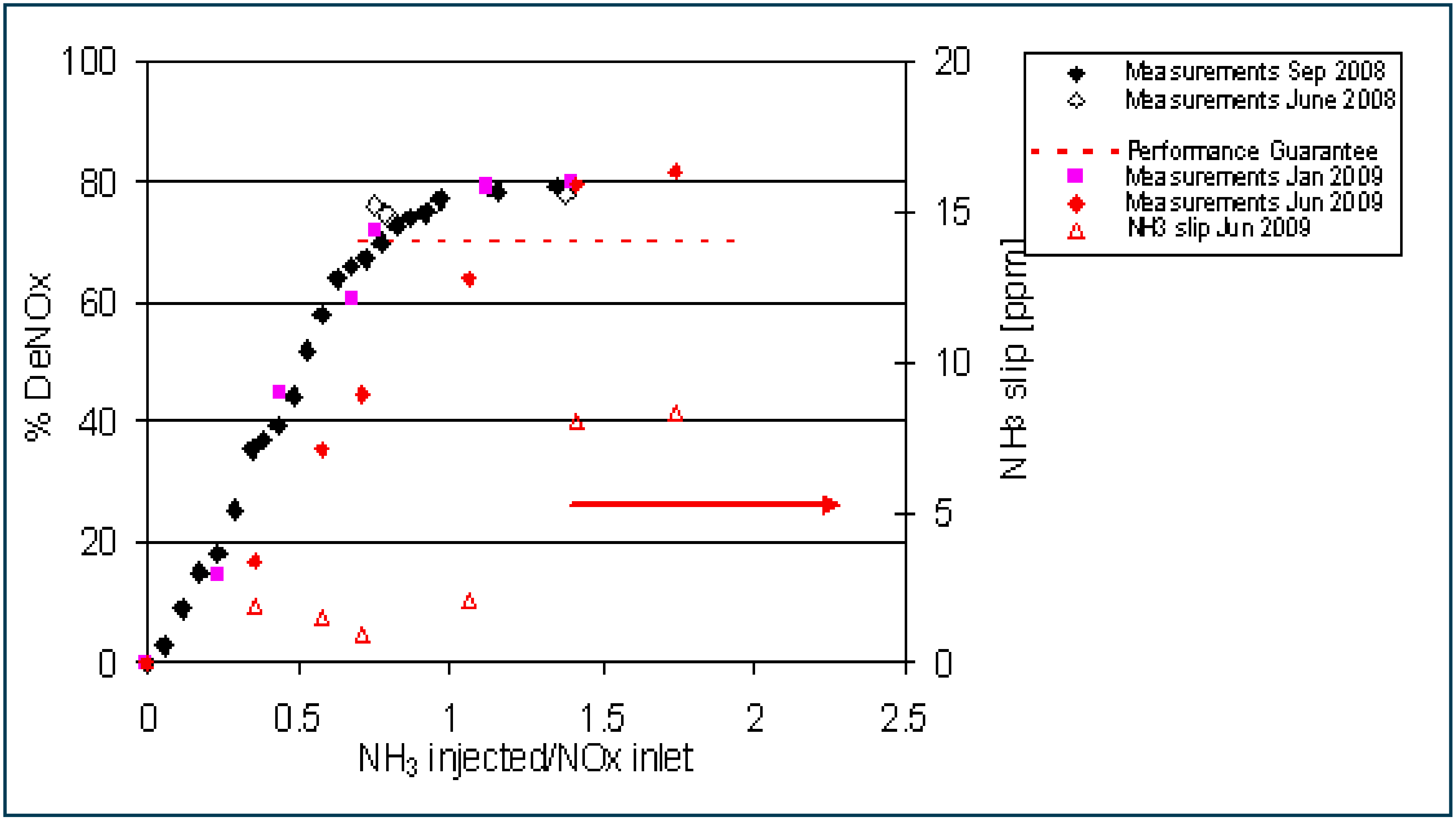
- Power Output – 5 Mwe
- Flue gas flow – 150,000 lbs/hr
- Flue gas temp. – 1,030 deg. F
- NOx inlet – 110 ppm
- DNX-029 Installed – June 2008

Performance:

- Daily Start ups
- Over 4,000 operating hours
- NOx Reduction - 80%
- Zero Catalyst Deactivation after expected initial activity loss

HALDOR TOPSØE

DNX-029HiTe Catalyst Field Experience



Thank you for your attention

HALDOR TOPSØE