Reinhold Environmental Ltd.

2010 NOx-Combustion Round Table & Expo Presentation

February 8 & 9, 2010 Chattanooga, TN

e·on | Engineering

Experience with Catalyst Regeneration

2010 NOx-Round Table, Chattanooga, TN
Workshop 14 - February 9, 2010

Dr. Peter Struckmann
Jürgen Brandenstein

Agenda

- Catalyst Regeneration Process
- Experience with Regeneration:
  - DeNOx Activity
  - Conversion Rate
  - Removal of Components from Inner Surface Area
  - Removal of Surface Layers
  - Plugged Channels / Pores
  - Mechanical Strength
- Regeneration Guarantees / Information / Testing
- Regeneration Outlook
- Summary
- Questions

Catalyst Regeneration - Terminology

- **Dry Cleaning**
  Removing of physical built up like fly ash by vacuuming / air lancing / vibrating typically on site in and ex situ

- **Washing (Rejuvenation)**
  Rinsing or soaking of catalyst with water or chemical solution to remove fly ash, water soluble blinding layers and catalyst poisons typically on site in and ex situ, also off site

- **Regeneration**
  Remove the above plus chemically bonded poisons, cleaning of the micro pore system with ultra sonic treatment and restore the active catalytic material typically off site

Ultrasonic Catalyst Regeneration - History

- 1997 - Idea was born at power plant Tiefstack (Vattenfall Hamburg, Germany)
- 1998 - Installation of a pilot regeneration plant at Tiefstack
- 1999 - Commissioning of first commercial regeneration plant in Wildeshausen, Germany
- 2001 - Foundation of SCR Tech, Charlotte, USA
- 2007 - Installation of Evonik's regeneration plant in Kings Mountain, USA
- 2009 - Commissioning of KC Cottrell's regeneration plant in Yeosu-si, Jeollanam-do, South Korea

Ultrasonic Catalyst Regeneration Plants

Catalyst Regeneration – Our Experience

- First regeneration project of a third party customer in 1998
- First regeneration project for our own fleet in 2000
- Since 2000 approx. 3,200 m^3 of E.ON catalyst has been regenerated
- Power plants: Ingolstadt, Scholven Unit B, Scholven Unit C, Scholven Unit D, Scholven Unit E, Scholven Unit F, FWK Buer, Staudinger Unit 1, Mehrum, Veltheim Unit 1, Veltheim Unit 2, Veltheim Unit 3, Heyden, Farge, Datteln, Maasvlakte
- Regenerated catalyst testing and consulting services for over 30,700m^3
- Multiple regenerations: 6 times honeycomb and 3 times plate type



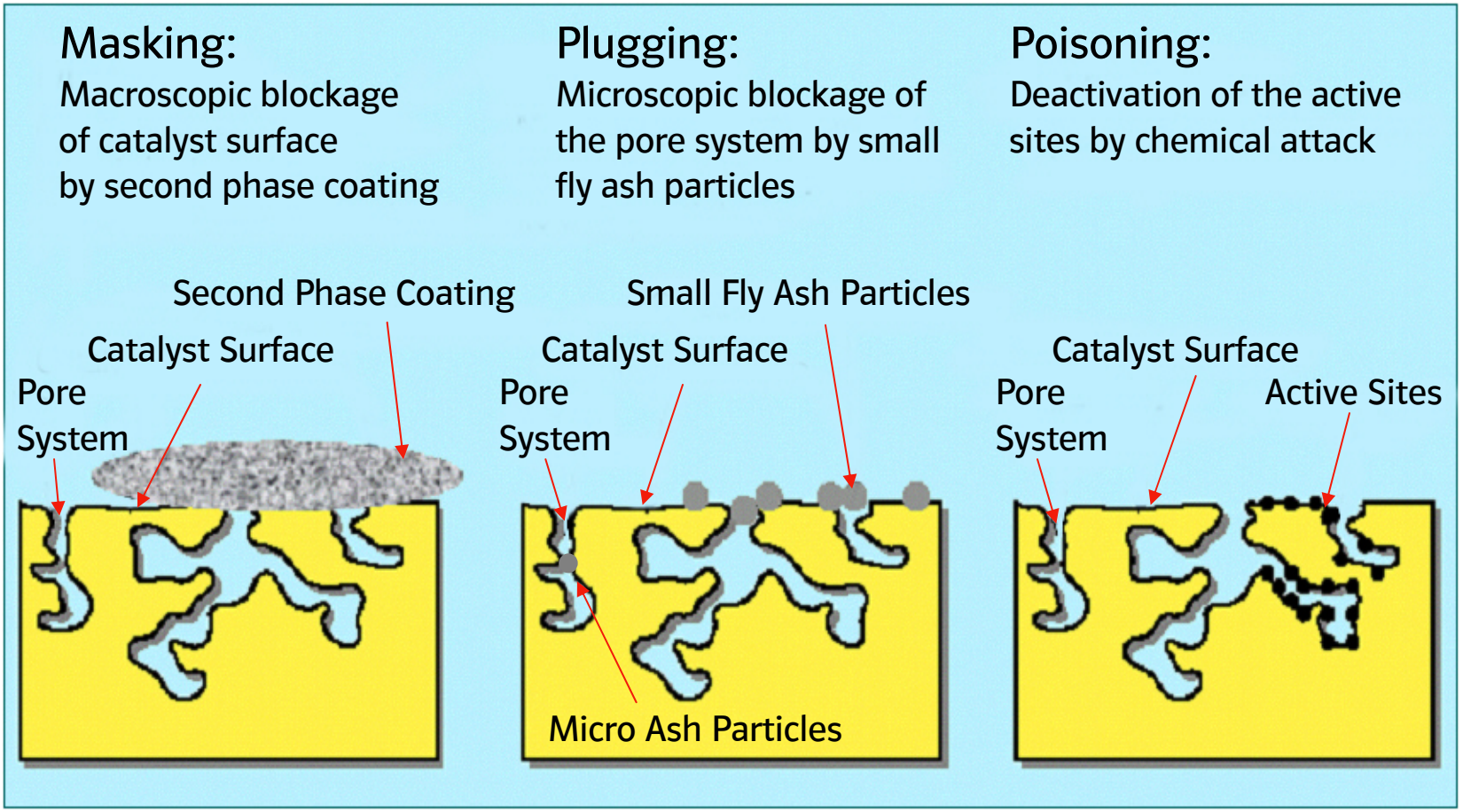






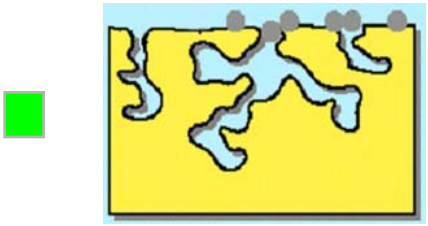


Catalyst Deactivation Mechanism



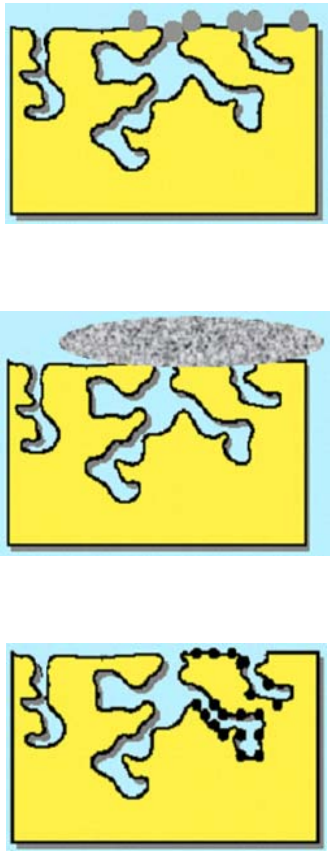
Source: Siemens

Catalyst Regeneration Step 1 – Dry Pre-cleaning



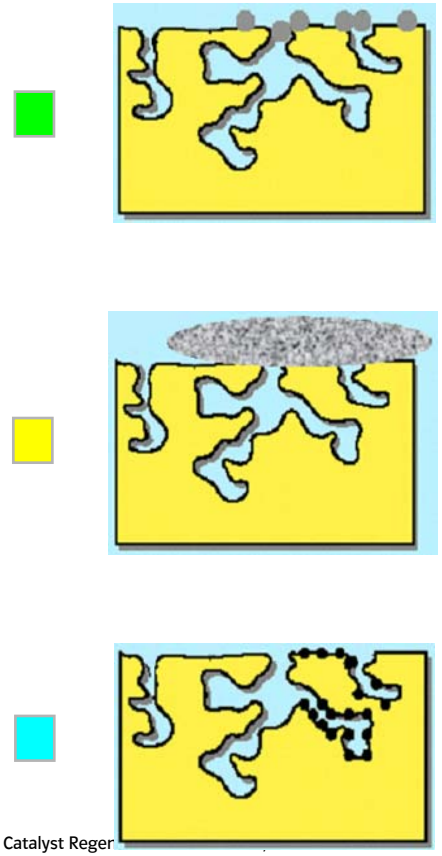
Catalyst Regeneration Step 2 – Pre-Washing/Chemical Cleaning

- PH controlled Pre-Washing for removal of residual fly ash
- Chemical Cleaning removing most of the catalyst poisons



Catalyst Regeneration Step 3 – Ultrasonic Treatment

- Ultrasonic step, deep cleaning of catalyst material including removal of micro-pore plugging, remaining blinding layers and even residual catalyst poisons



Catalyst Regeneration Step 4 – Washing / Chemical Cleaning

- Removal of remaining chemically bound catalyst poisons
- Preparation of Re-Impregnation of active components

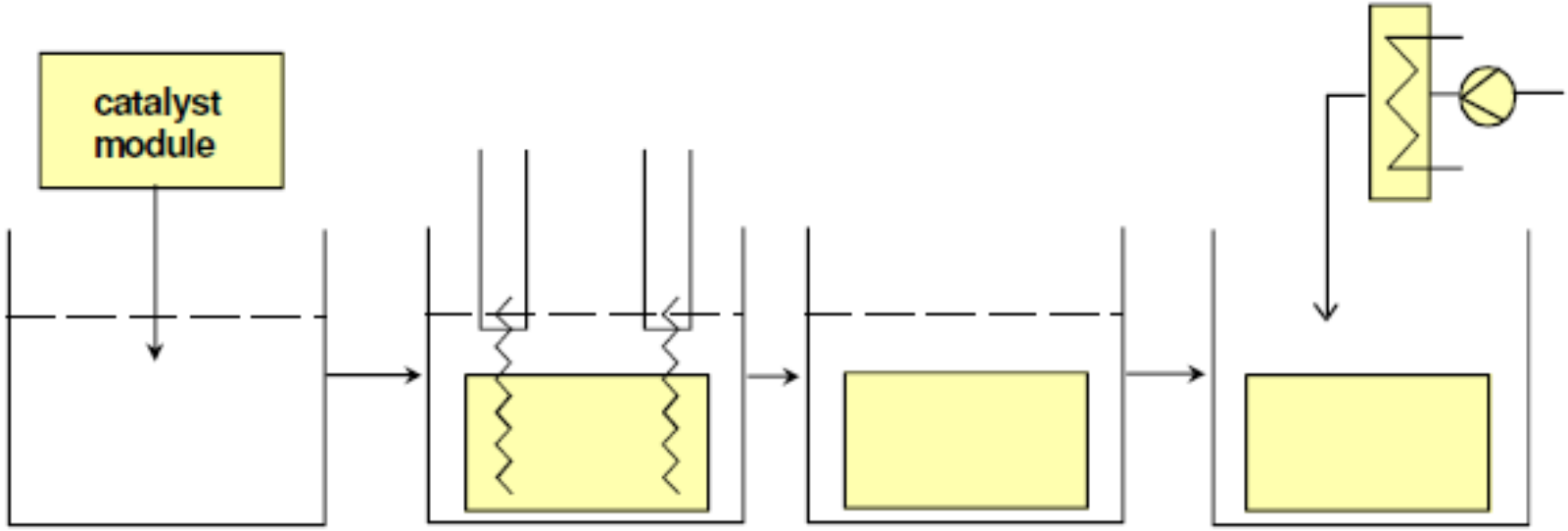
Catalyst Regeneration Step 5 – Re-Impregnation

- Re-impregnation of active components like V_2O_5

Catalyst Regeneration Step 6 – Drying

- To accelerate the start-up ramp of the SCR
- To reduce weight for module shipment

Catalyst Regeneration Process Flow Sheet



pre-washing station

- to soak catalyst material
- to dissolve catalyst poisons

ultrasonic bath

- to remove surface layers
- to clean plugged channels

washing station

- to remove soluble catalyst poisons
- to impregnate with active components (e.g. V_2O_5)

drying station

- to accelerate the start-up ramp of the DeNOx plant
- to reduce weight for module shipment

Catalyst Regeneration Plant

Agenda

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- Experience with Regeneration:
  - DeNOx Activity
  - Conversion Rate
  - Removal of Components from Inner Surface Area
  - Removal of Surface Layers
  - Plugged Channels / Pores
  - Mechanical Strength
- Regeneration Guarantees / Information / Testing
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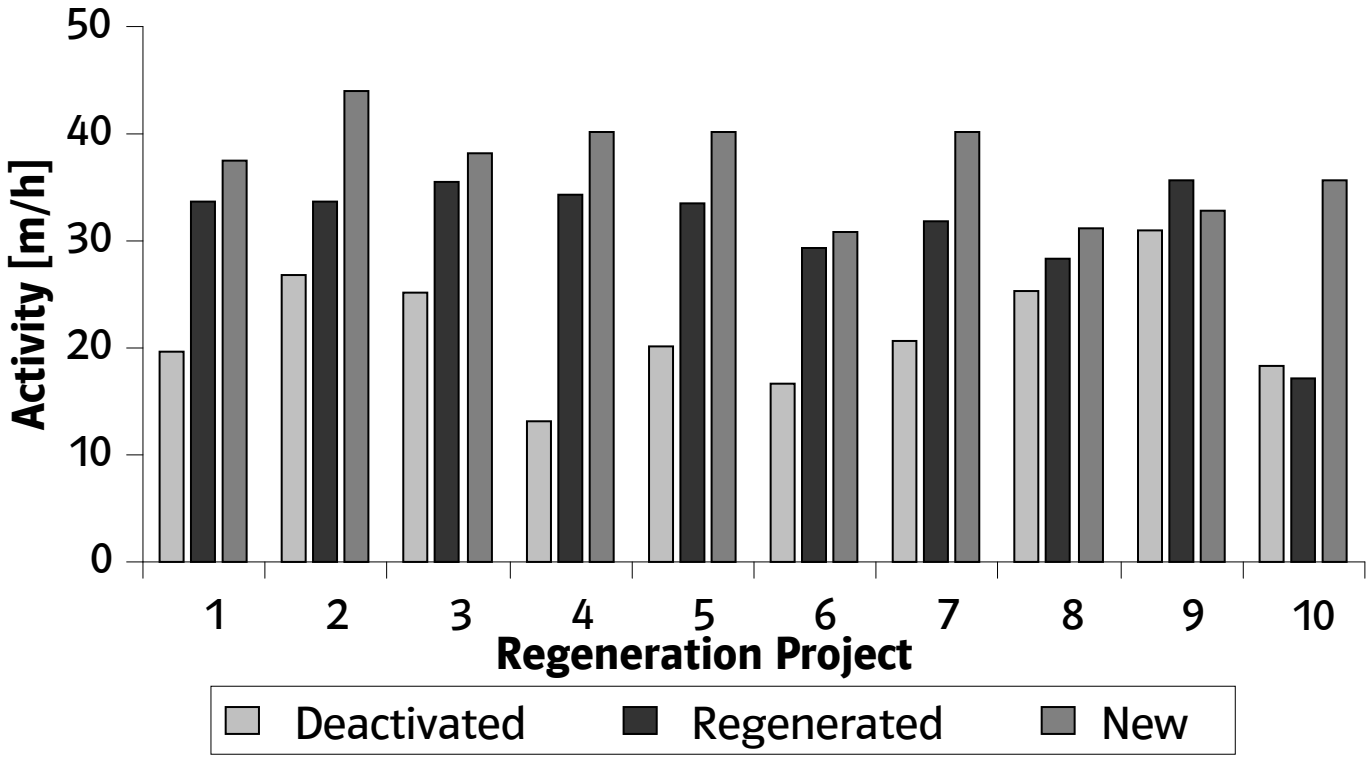
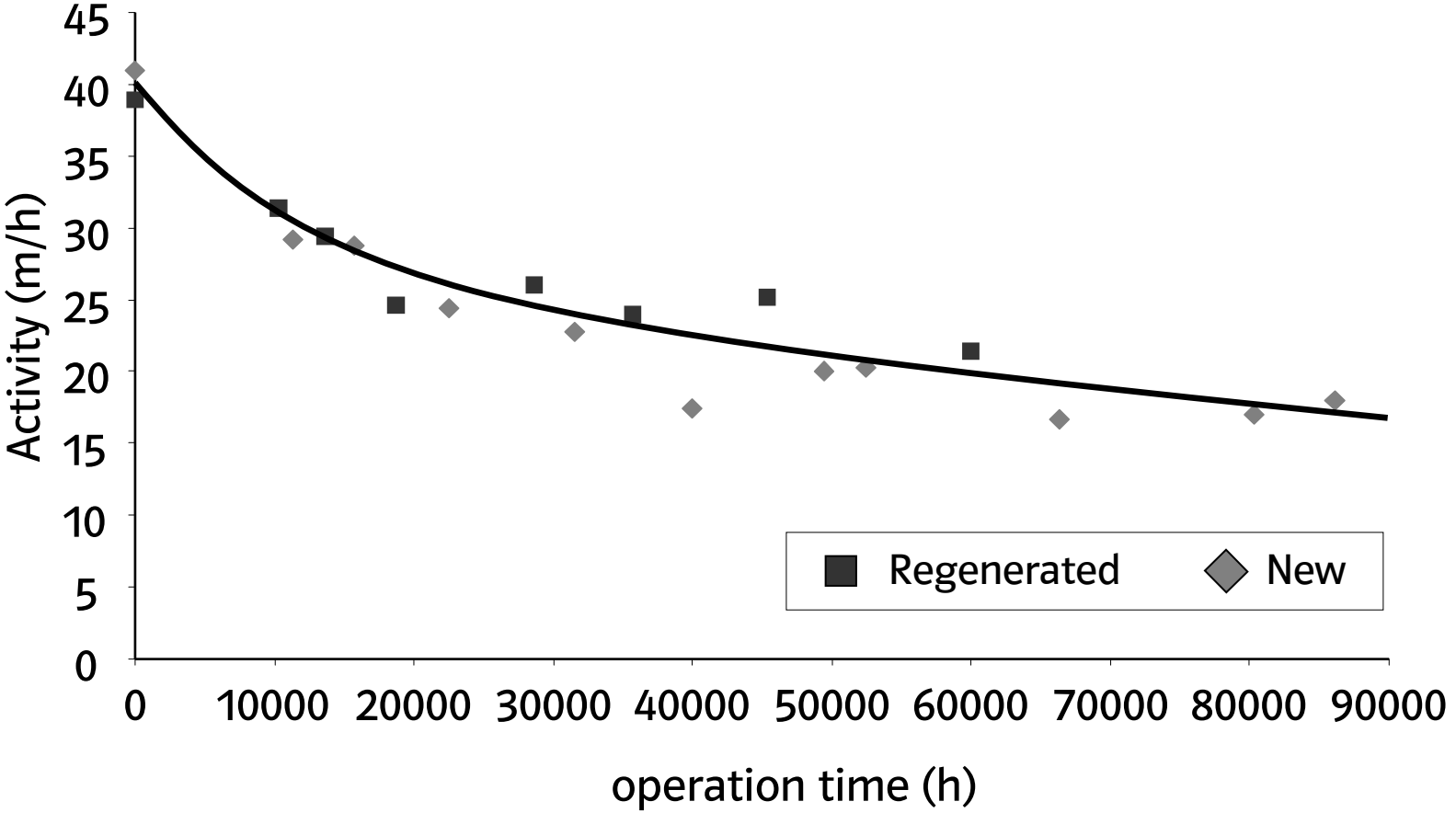
Experience with Regeneration – DeNOx-Activity

- Typical results for regenerated catalyst: Activity > 90% of the new material
- In some occasions: regenerated catalyst activity higher than of the new material



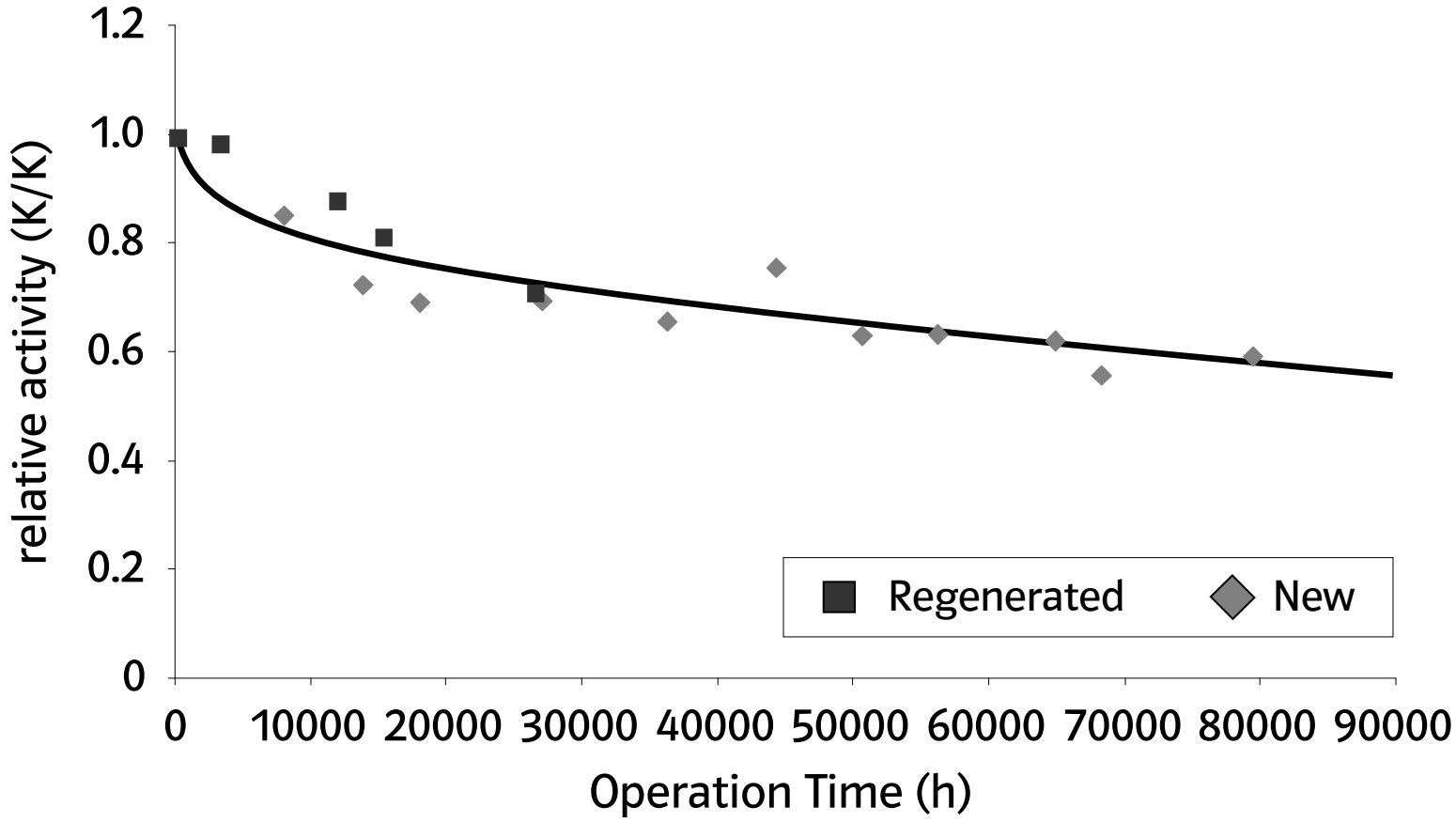
Operational Experience with Regeneration Catalyst

- BHK C' plate type catalyst, Unit A



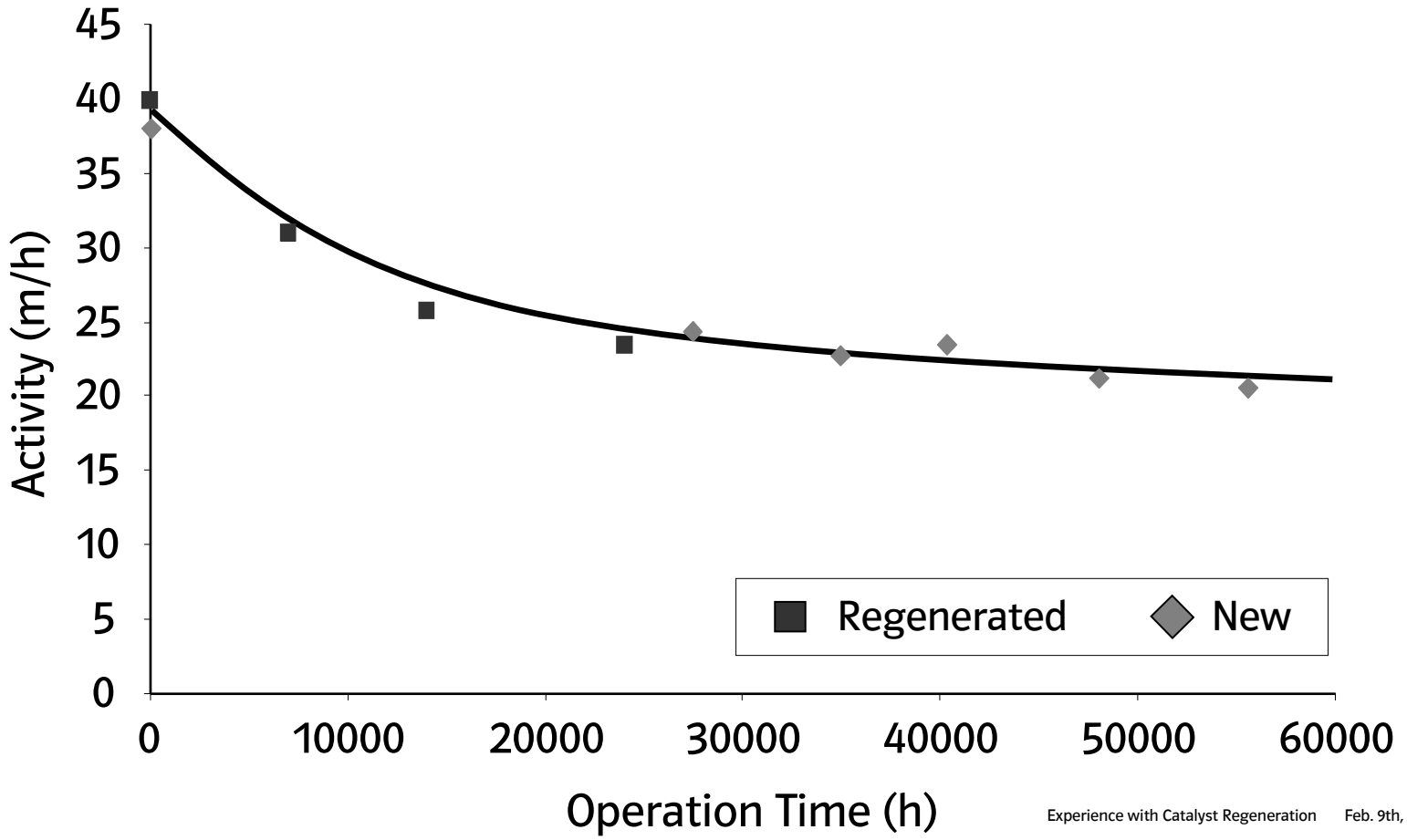
Operational Experience with Regeneration Catalyst

- BHK X6 plate type catalyst, Unit B



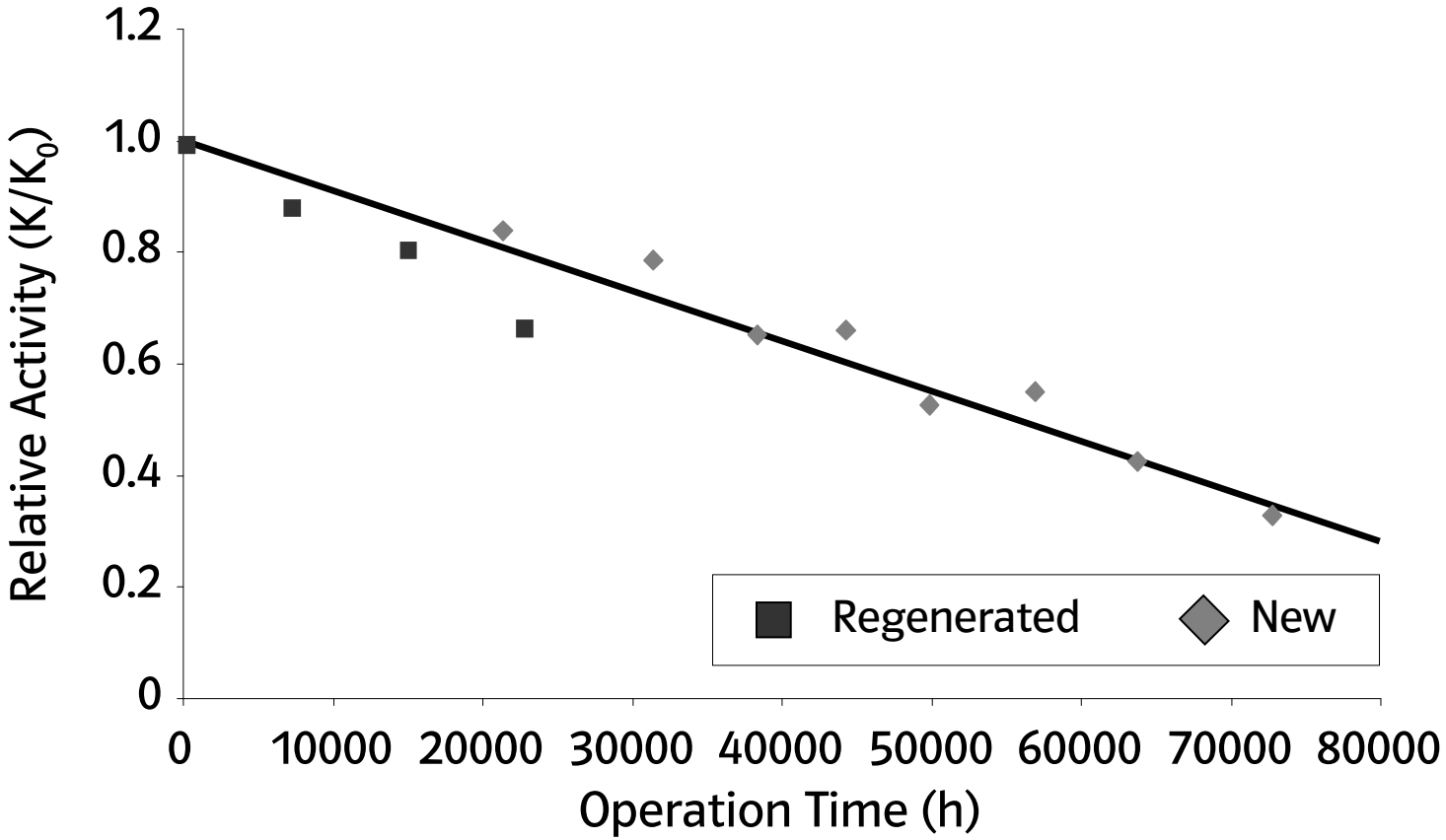
Operational Experience with Regeneration Catalyst

- Siemens plate type catalyst, Unit C



Operational Experience with Rejuvenated Catalyst

- Washing process in an E.ON plant, Siemens Honeycomb catalyst

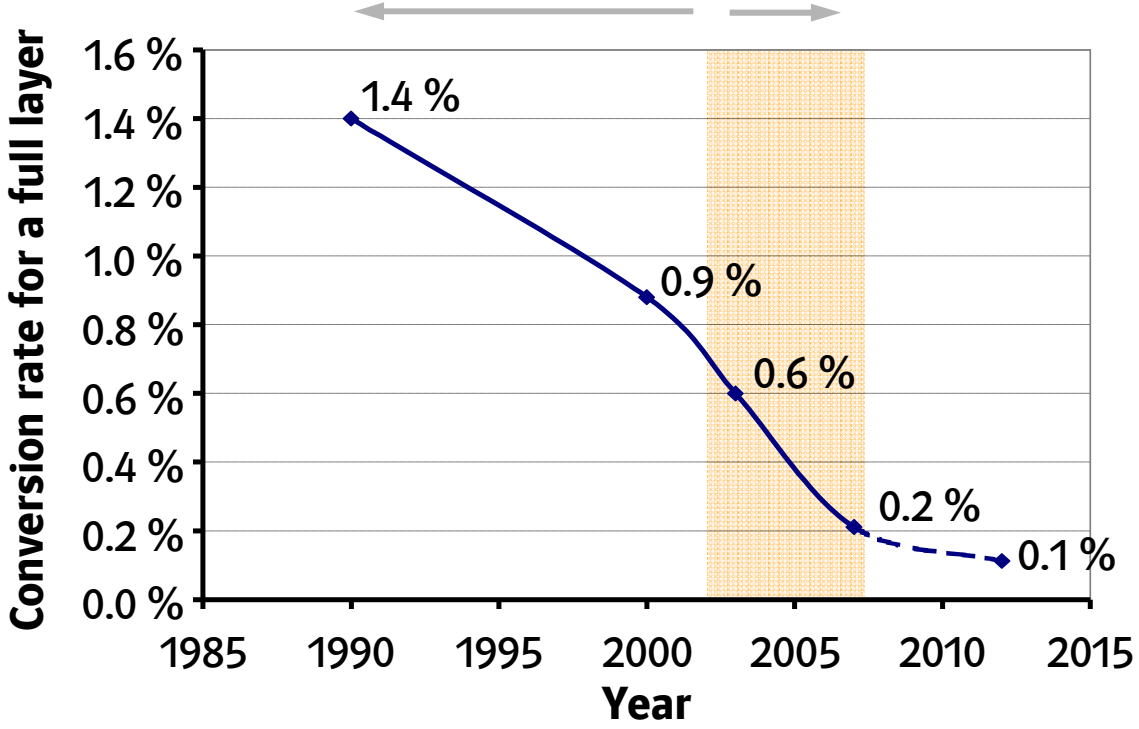


Conversion rate - History

- Blue plume issue forced the catalyst vendors to lower the SO_2- Oxidation rate of the catalyst material

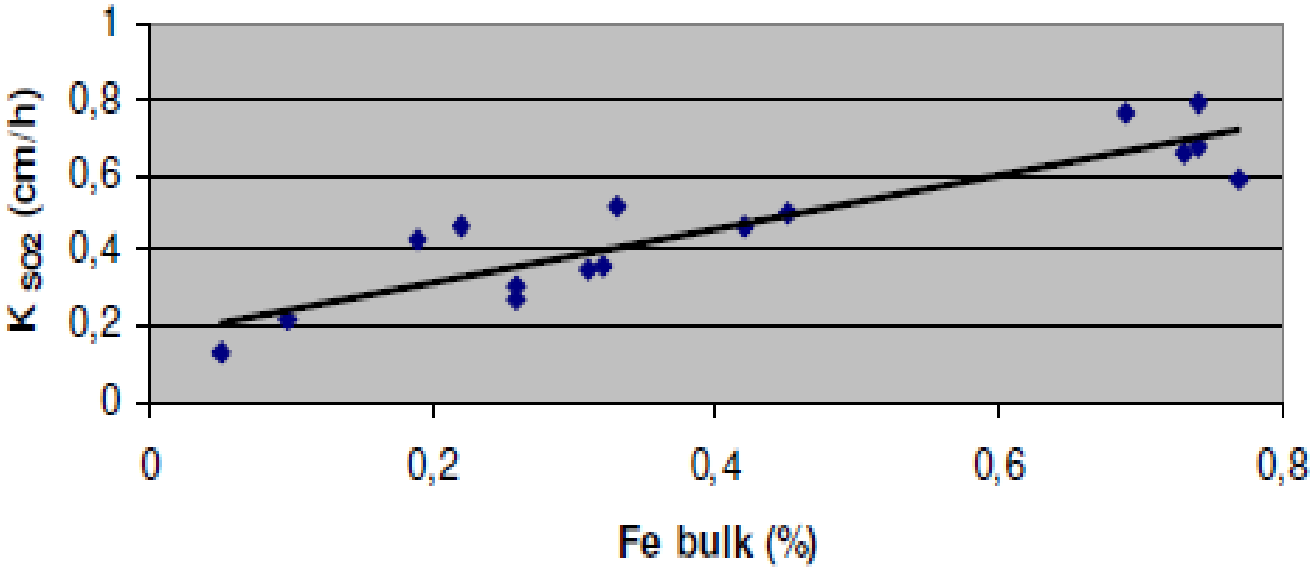
Decreasing conversion rate below new material possible with regeneration

Maintaining / Reducing conversion rate down to new material levels is challenging



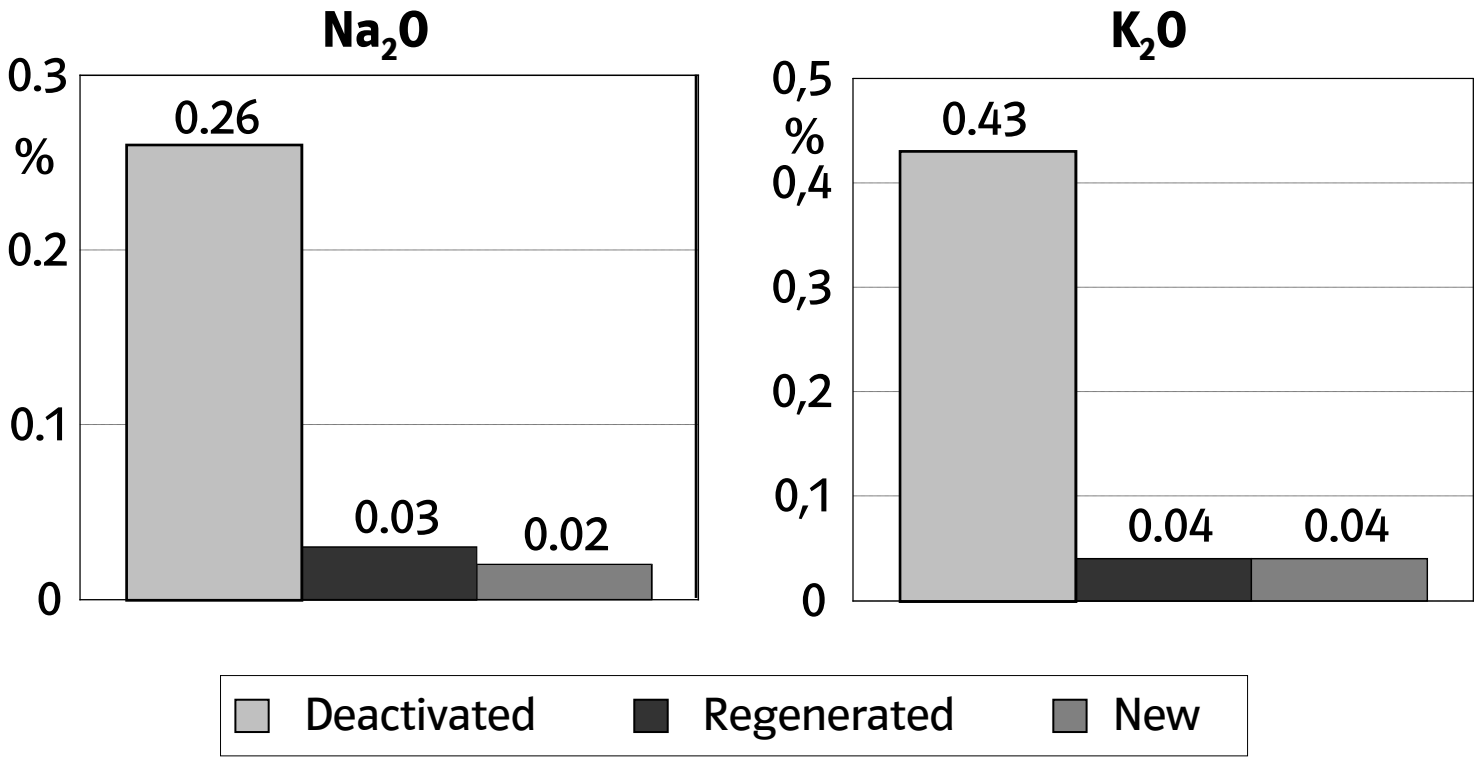
Experience with Regeneration – Conversion Rate

- Correlation between SO_2/SO_3 conversion rate and iron uptake during regeneration (honeycomb catalyst)



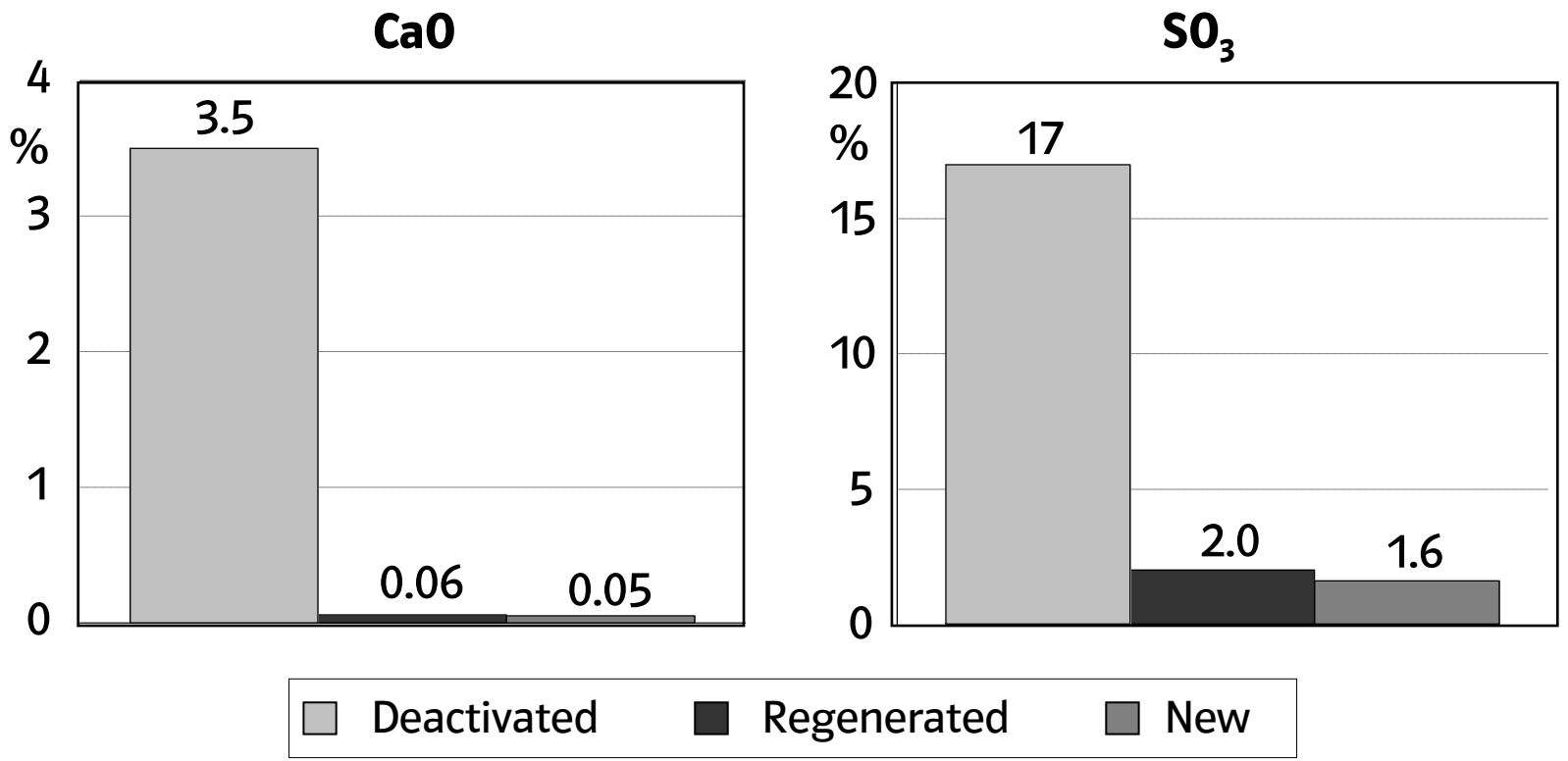
Experience with Regeneration – Removal of Compounds from Inner Surface Area

- Removal of intruded alkali metals (bulk material)



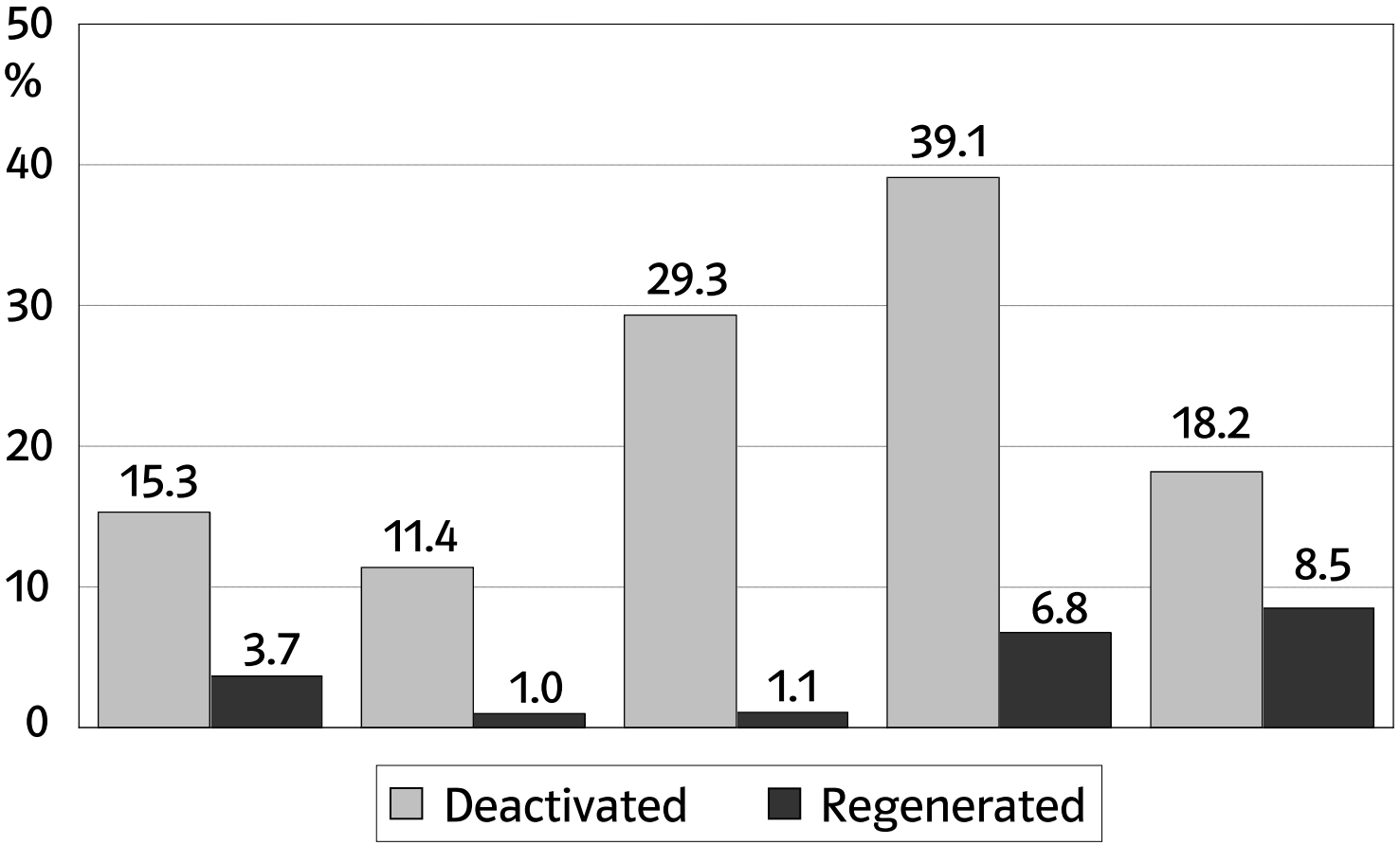
Experience with Regeneration – Removal of Surface Layers

- Removal of blinding layers (surface analysis)

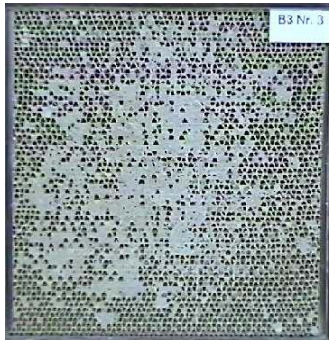


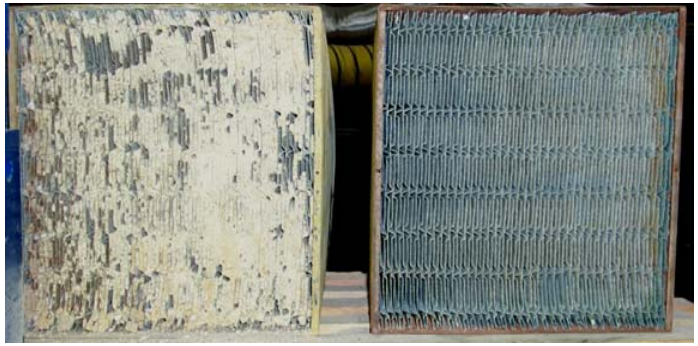
Experience with Regeneration – Plugged channels

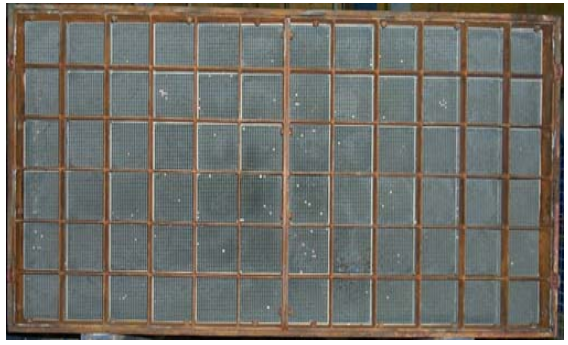
- Number of plugged channels before and after Regeneration [%]



Experience with Regeneration – Plugged channels / pores







	BET m^2/g	pore vol. cm^3/g	pore diam. Å
1st layer, inlet – deact.	45.31	0.176	147,79
1st layer, outlet – deac.	50.92	0.196	142.33
1st layer, inlet – regen.	64.02	0.232	131.93

Experience with Regeneration – Mechanical Strength

- Mechanical strength is one of the most important parameters used to evaluate if a catalyst is suitable for regeneration

- No meaningful standard test to evaluate mechanical strength for all catalyst types
- Most commonly used for:
  - Honeycomb type catalyst: the compressive strength test
  - Plate type catalyst: the bonding strength test

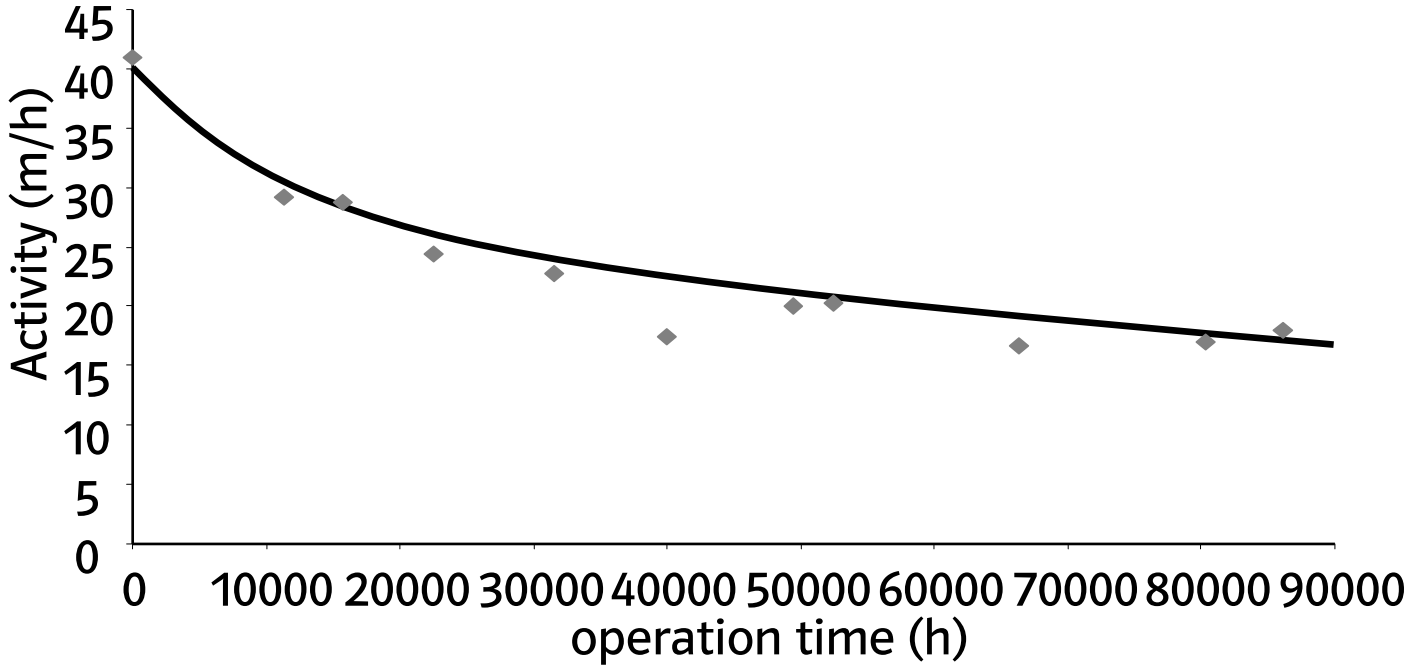
Experience with Regeneration – Mechanical Strength

- Reliable results need a statistical approach, adaptability to SCR operations questionable (weakest catalyst according to strength test was the only one surviving in a high dust application of a plant burning 30% ash coal (FWK))

- If a catalyst was mechanically sturdy to be regenerated, we never saw mechanical failure during transport, installation, start up or operation

Information Provided to the Regenerator

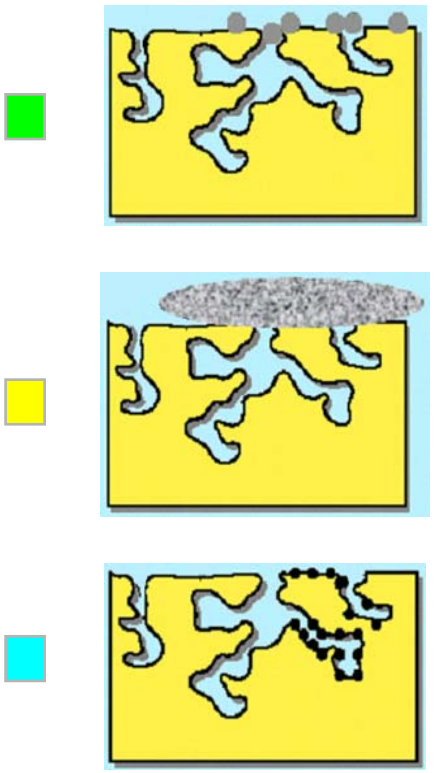
- Catalyst Information: catalyst type, operating time, number of modules, geometrical data such as length, with and pitch,
  - Activity and deactivation rate
  - Initial conversion rate / conversion rate over time



Chemical Composition of Catalyst

- Chemical composition of new and deactivated catalyst

		new	bulk		surface	
			inlet	outlet	inlet	outlet
SiO_2	%	9.0	8.7	9.4	27.0	19.6
Al_2O_3	%	0.60	0.58	0.62	5.4	3.8
Fe_2O_3	%	0.05	0.42	0.33	0.58	0.48
TiO_2	%	78.0	76.8	76.8	48.7	63.0
CaO	%	0.95	0.97	1.08	1.92	1.42
MgO	%	0.11	0.13	0.14	0.19	0.21
BaO	%	0.10	0.15	0.10	0.09	< 0.03
Na_2O	%	0.05	0.06	0.04	0.30	0.11
K_2O	%	0.07	0.23	0.14	0.45	0.12
SO_3	%	0.85	1.28	1.06	9.2	3.6
P_2O_5	%	0.05	0.09	0.07	0.41	0.27
V_2O_5	%	0.35	0.36	0.34	0.63	0.68
WO_3	%	9.6	9.8	9.5	4.7	6.2
As	ppm	20	1814	1392	1133	1003



Operational Data

- <u>Flue Gas Information</u>
  Temperature, Volume Flow, NOx inlet, NOx outlet, SO_2 & SO_3 inlet, O2 content, water content, …
- <u>General</u>
  Start-up Year, Reactor Design, Number of Reactors, Layers per Reactor, Layer to be Regenerate, …

- Who handles removing / installation of the layer?
- Who handles transportation?
- Is storage needed / where is the layer being stored?

Regeneration Guaranties

- Minimum activity after regeneration — K_{regen} = XX [m/h]
- Maximum SO_2/SO_3 conversion rate after regeneration — $K_{SO2/SO3}$ = XX [%]
- Maximum pressure drop — p ≤ XX [mbar]
- Ask for material guarantee: activity after e.g. 16,000 hrs — $K_{regen.16,000}$ = XX [m/h]
- Ask for extreme case scenarios:

  (1) Conversion Rate Max. with corresponding Activity

  (2) Activity Max. with corresponding Conversion Rate

Guarantee Testing

- Independent 3rd party
- Full scale bench testing
- Testing under actual plant conditions
- Sampling regularly, e.g. every 40m³
- Guarantee testing conditions:
  - Activity (K): **NH_3 / NOx ratio = 1.0**
  - Conversion rate ($K_{SO2/SO3}$): **NH_3 / NOx ratio = 0.0**
  - SO_3 inlet conc. defined for: **K and $K_{SO2/SO3}$**
  - Test Accuracy: Activity **+/- 1.0 m/h**
  - Test Accuracy: Conversion Rate **+/- 0.05%**

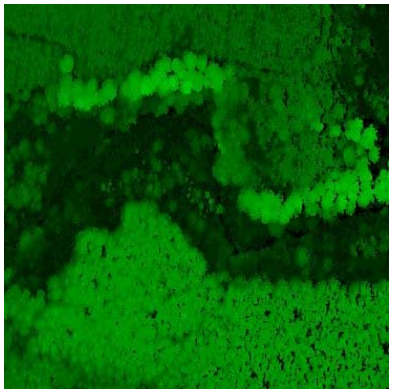
Test regeneration is a helpful tool!

Catalyst Regeneration - Outlook

- Continuous process improvement by regeneration companies to lower conversion rates while maintaining / increasing activities

- In Germany research projects for:
  - Regeneration optimized for Hg – oxidation
  - Regeneration optimized for Co-combustion

- ?



Summary

- Regain (most of) initial activity
- Low/Moderate SO_2 conversion rate
- Removal (complete) of intruded soluble poisons such as Na_2O, K_2O…
- Removal of As- and P- compounds by special treatment
- Complete removal of surface layers
- Complete cleaning of plugged channels
- Similar activity deactivation rates – over 50,000 h of experience
- Avoid catalyst disposal costs (hazardous waste)
- Lower investment cost compared to new catalyst