REINHOLD ENVIRONMENTAL Ltd.

2014 NOx-Combustion Round Table & Expo Presentations

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Current Status and Challenges of Mercury-Oxidation Testing of SCR Catalyst

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2014 NOx-Combustion Round Table, February 10, Charlotte

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Overview

Key facts about Mercury

Mercury in fuels, legislation

Mercury in combustion and power plan

Mercury at SCR catalyst

- Influence on Hg oxidation
- factors: known and unknown

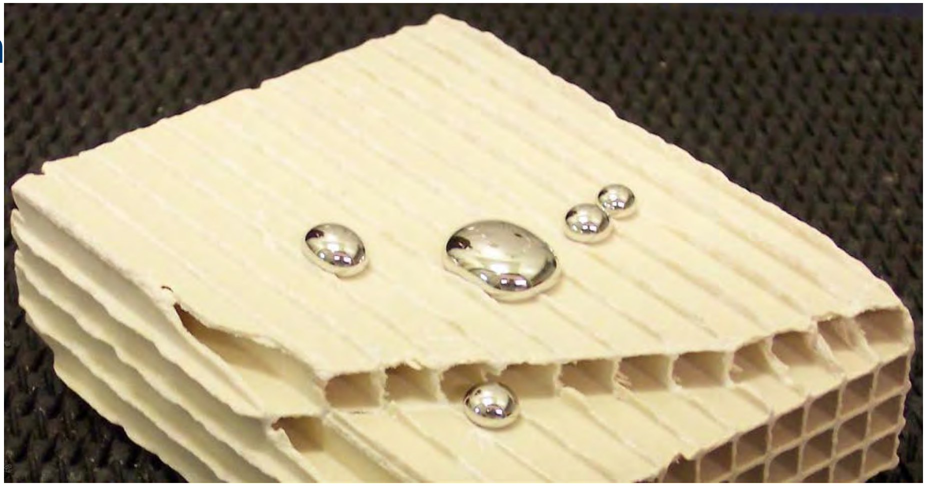
Why testing catalysts?

How testing catalysts?

- schematic sketch
- test methods, sample size

Where do we stay?

What´s next?



Key facts about mercury

Mercury Hg is neurotoxic

passes blood-brain barrier and placental barrier

→ especially vulnerable: kids and pregnant women

Anthropogenic release due burning fossil fuels

→ major source: generation of energy

Global Mercury pool increasing steadily since industrialization

→ tripled since then

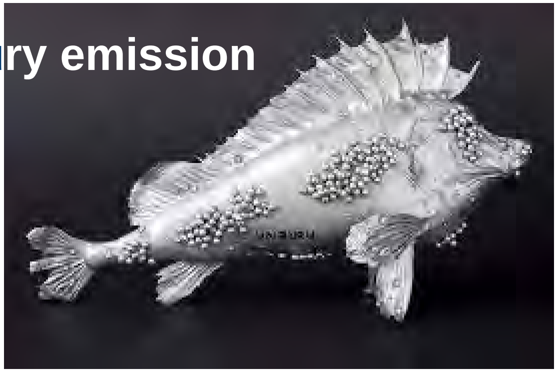
Global distribution of emitted mercury

→ resistant time in atmosphere up to 1 year

Worldwide large exertion to curb mercury emission

→ Minamata Convention on Mercury

→ need for best available technology



Mercury in fuels

Mercury in almost every used fuel:

biomass → especially sewage sludge, peat

waste → wide range

wood → small amount ~ 0.05 mg/kg

coal *American bituminous coal*

→ wide range 0.08 < Hg < 0.22 mg/kg **[Toole-O'Neil, (1998)]**

worldwide average

→ 0.1 mg/kg (in flue gas ~ 20 µg/m^3*)
sulfur rich coals often mercury rich (Hg-S-compounds)

*(5 m^3 flue gas/1 kg coal)

Legislation

US EPA „Mercury is a hazardous air pollutant“

Stricter legislation is expected in 2015/2016

→ removal of 95 % (2015), 97 % (2016)

→ limit ~ 1.5 µg/m³ yearly average value

→ not possible to reach without control and planning

Mercury in combustion

Hg is volatile → at boiler temperature of 1,000 – 1,500 °C

complete release of organic and inorganic fixed Hg

After combustion

→ all Hg only elemental (Hg^0)

very fast cooling on flue gas path

→ partly oxidation of Hg (Hg^{2+})

→ Hg Adsorption at particles (Hg^{par})

Properties of different mercury species require different deposition method:

Hg^0 not water soluble – adsorption on activated carbon

Hg^{2+} high water soluble – FGD

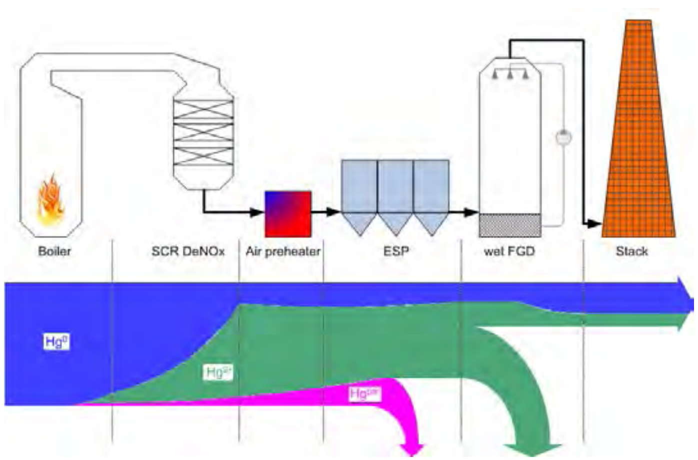
Hg^{par} filtering separation – ESP

Mercury in power plant

Hg oxidation and reduction at SCR catalyst, ESP, FGD

Hg oxidation at conventional DeNOx catalyst: wide range

Hg reduction in FGD: Remission – release through stack



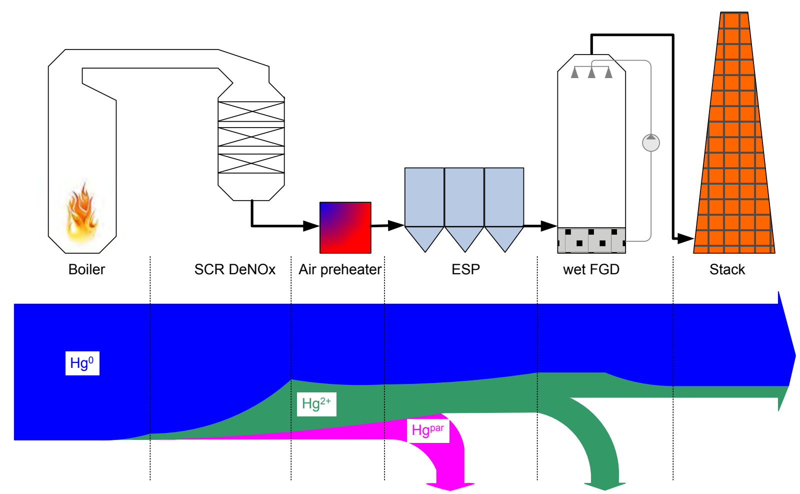


Fig. A: SCR catalyst with high efficiency in Hg oxidation

Fig. B: SCR catalyst with low efficiency in Hg oxidation

→→→Great importance of mercury oxidation at SCR catalyst

Mercury Oxidation at SCR DeNOx catalyst

Requirements for high mercury oxidation at SCR catalyst:

→ enough resistance time — resistance time ↑

→ enough active surface — active surface ↑

→ presence of oxygen — min 2 vol.%

→ presence of halogenides (Cl_2, Br_2, …)

Influences on mercury oxidation

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Known factors for high mercury oxidation at SCR catalyst:

Temperature	T ↓
Oxygen content	> 2 vol.% (indirect influence)
Halogenide content	Halog.↑
competitive reaction	NOx reduction ↓
ammonia content	NH_3 ↓
sulphur dioxide content	SO_2 ↓ (newer lit.: reverse results)
water content	H_2O ↓
low or no halogenides	adsorption of Hg at catalyst (abrupt release possible)

Influences on mercury oxidation

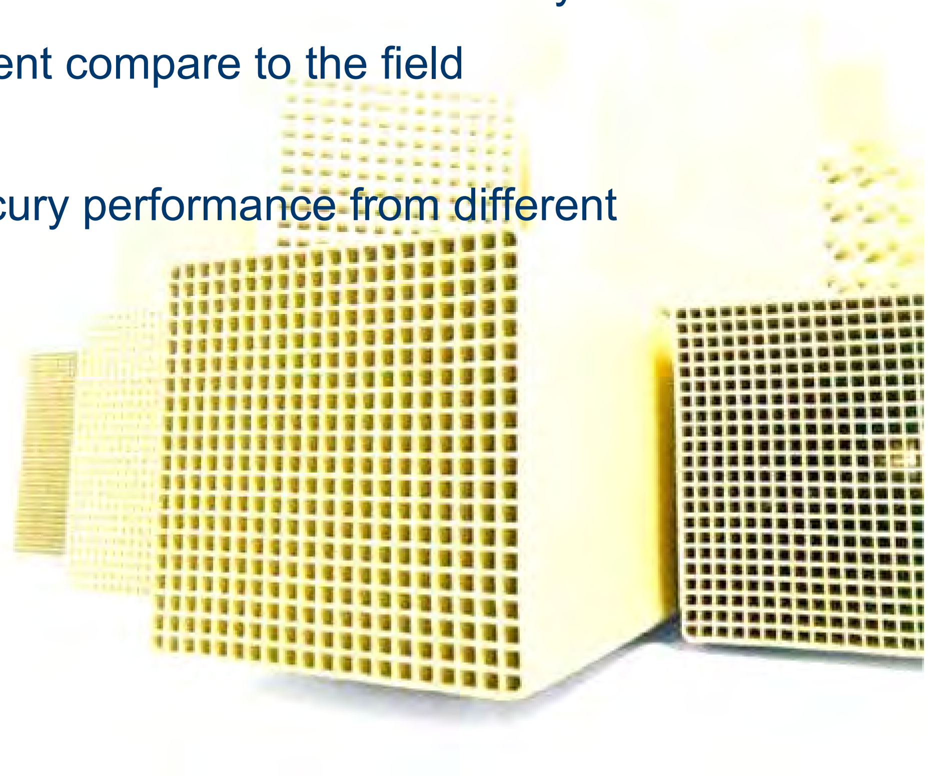
Partly unknown influencing factors

on Mercury-Oxidation at SCR DeNOx catalyst:

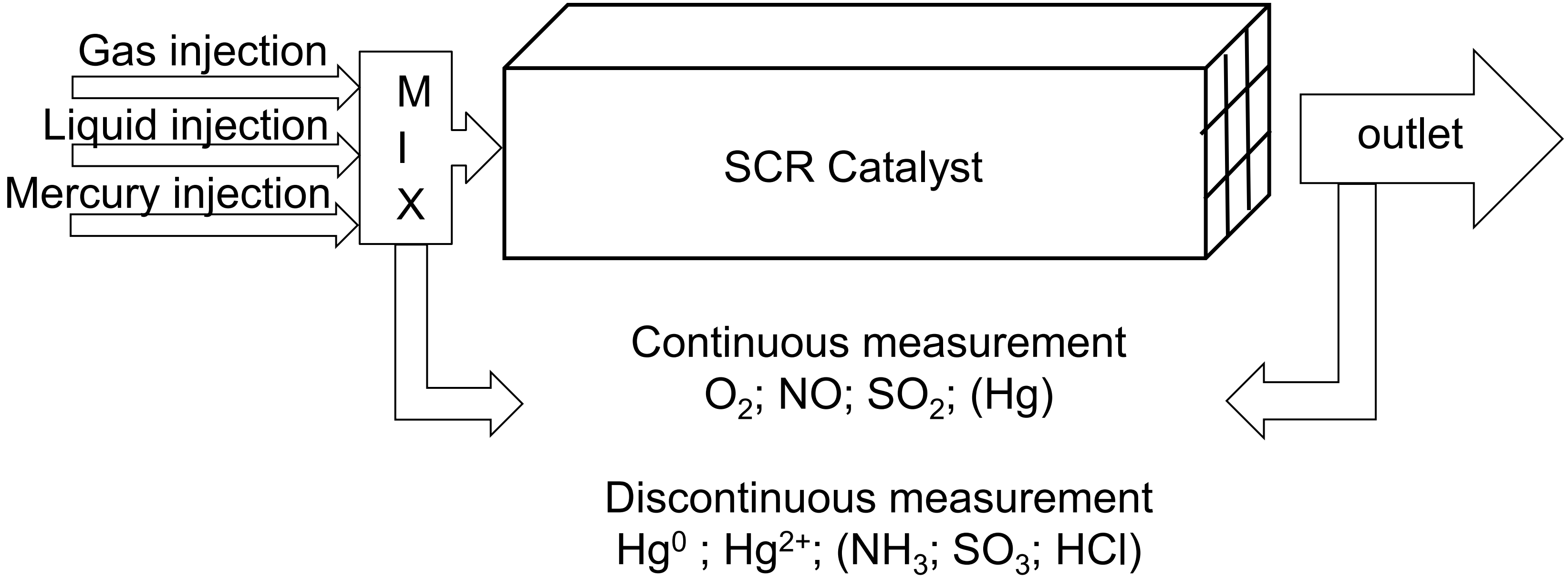
SO_3	seems not to influence Hg oxidation
NO	is known to rise Hg oxidation
NO_2	is not well investigated yet, seems to promote Hg reduction
CO	comes into investigation focus, seems to influence Hg oxidation
CO_2	seems not to influence Hg oxidation

Why should we test catalysts for mercury oxidation?

- Not a 1:1 correlation between NOx activity and Hg Oxidation
- The aging of the catalyst effects both in a different way
- More controlled environment compare to the field (Fly ash)
- Direct comparison of mercury performance from different catalyst samples



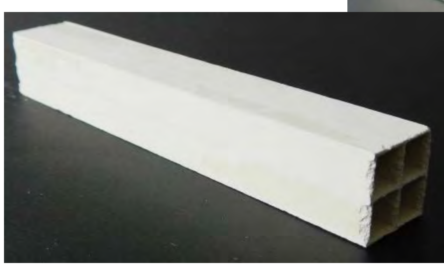
Schematic sketch of mercury test set up

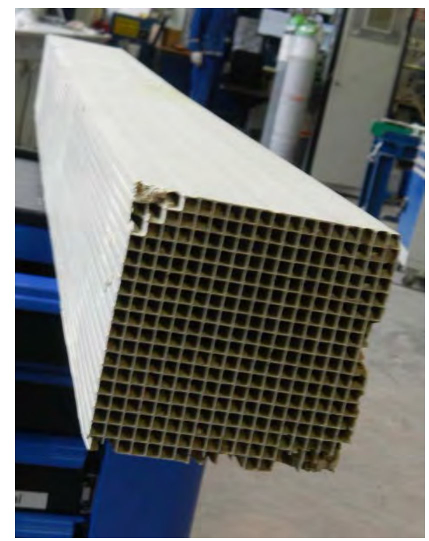


- Temperature controlled environment (200 to 450 °C)
- Digital multi component gas and liquid mixing system → close to plant parameters
- Measurement up and down stream of catalyst
- NOx removal and SO_2/SO_3 conversion rate testing optional

Sample sizes

Micro reactor 2x2 Cells 100mm long	Semi Scale 5x5 Cells 200 – 500mm long	Bench Scale 20x20 Cells Full size – 1350mm





Mercury oxidation measurement

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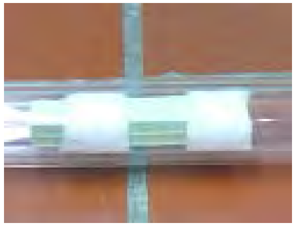
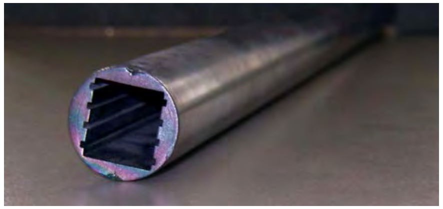
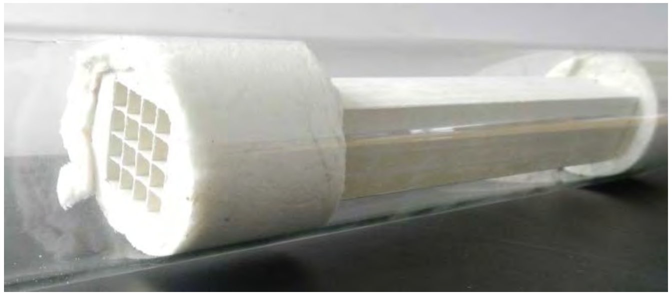
Catalyst preparation for micro tests:

– cutting the catalyst (honeycomb: band saw
plate type: mechanical shears)

– placing the catalyst (honeycomb: fixed with glass wool
plate type: fixed in special fixture)







From where to cut the sample to be representative?

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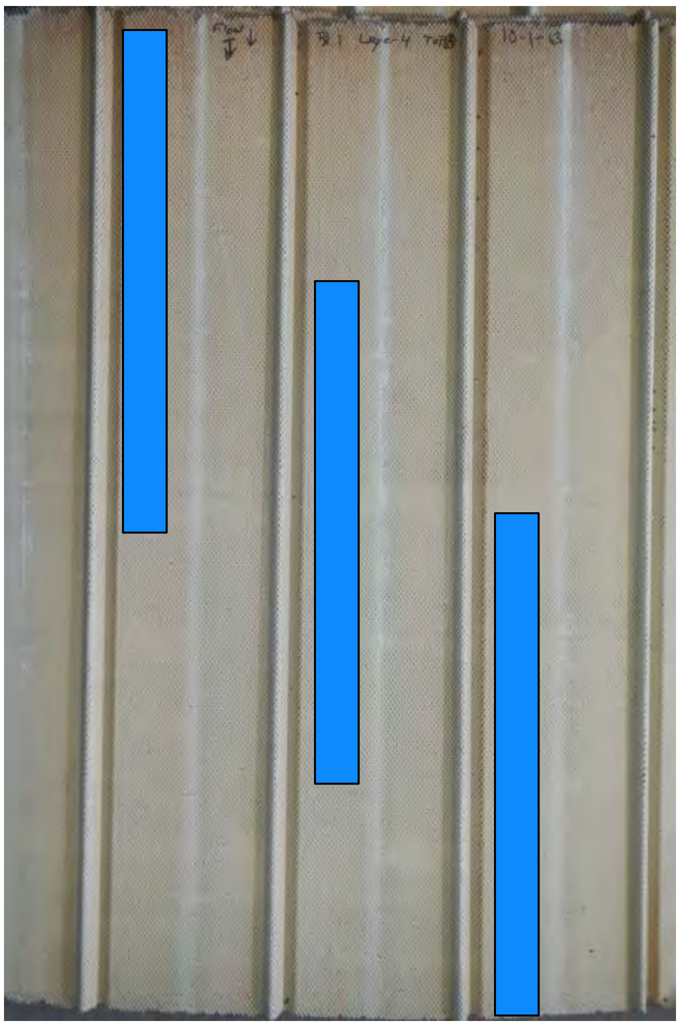


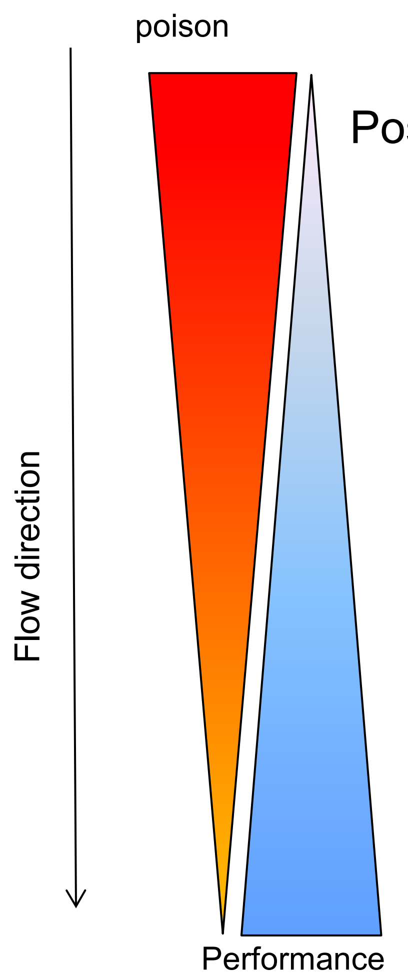
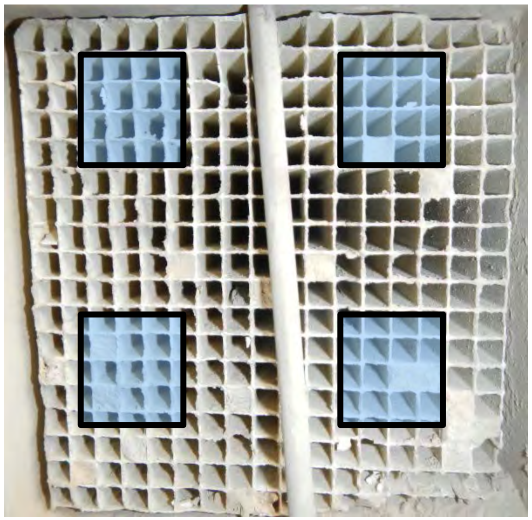


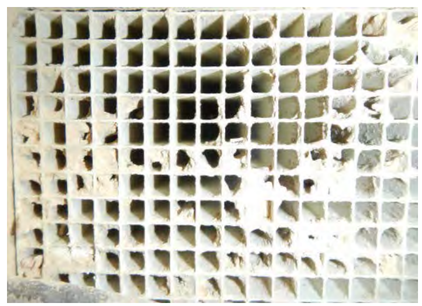
Plate type catalyst

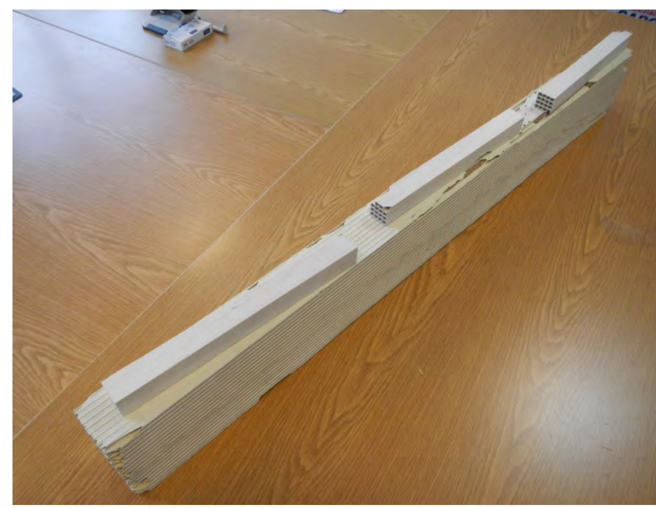
Position of the test coupons effect the result

From where to cut the sample to be representative?

honeycomb catalyst





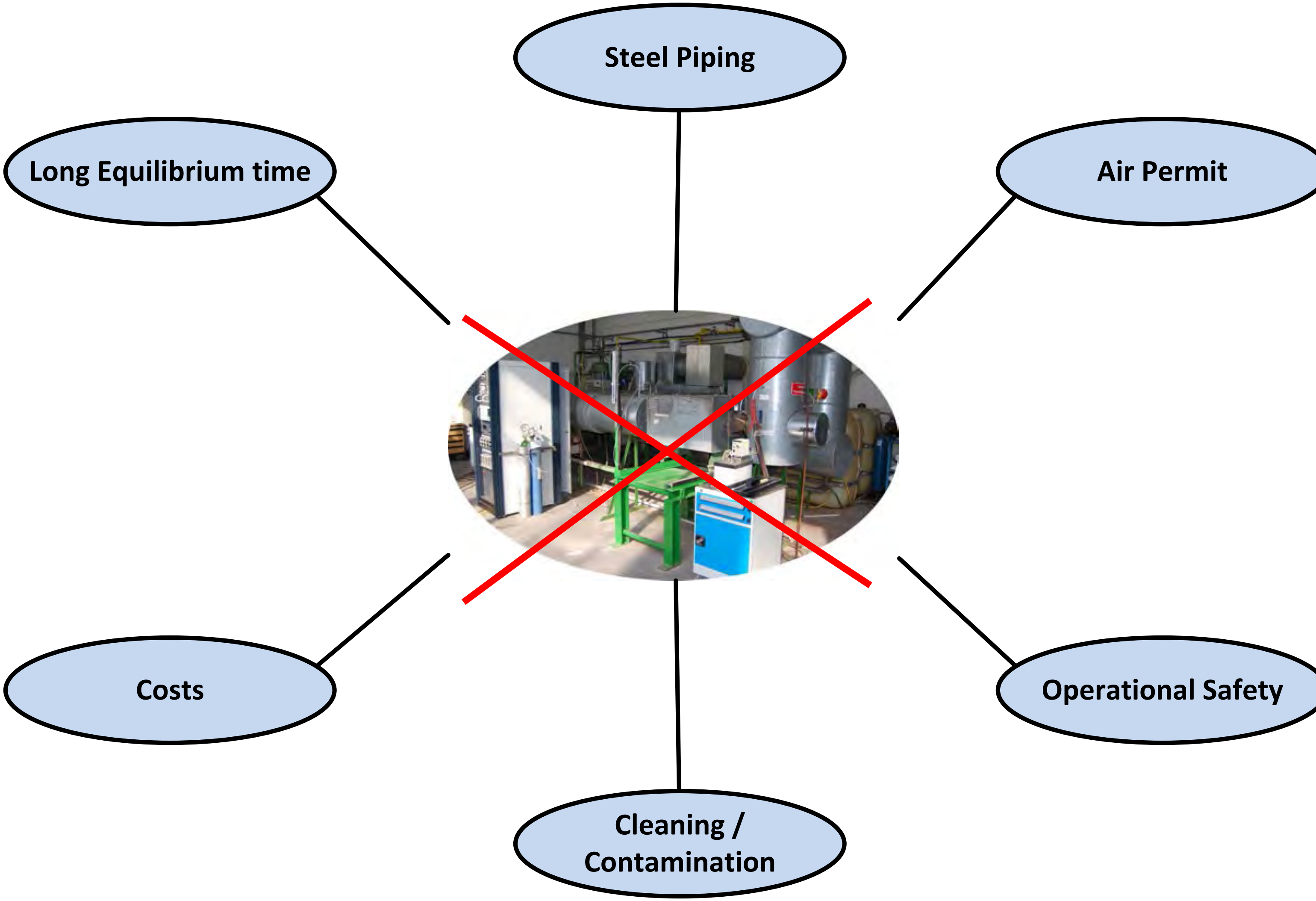


Adjustable Parameters for catalyst testing on mercury oxidation

parameter		Real SCR	Micro standard	Range micro
Temperature	[°C]	320 – 420	350 / field	250 - 430
LV	[Nm/s]	2 – 4	0.6	0.3 – 2.0
Length	[mm]	500 – 1,350	300	100 – 450
O_2	[vol-%, dry]	2.5 – 4.5	4.0	0 – 10
H_2O	[vol-%]	6 – 10	10	0 – 20
NO	[ppmvd]	10 – 900 **	75	0 – 500
$\alpha = NH_3/NO$		α = 0.02 – 0.93 **	α = 0.2	α = 0 – 1.2
SO_2	[ppmvd]		1,000	0 – 4,000
Hg^0 / Hg^{2+}	[µg/m³]	0 – 100 total	80 / 0	50 – 100
HCl	[ppmvd]	3 – 100	60	0 – 80
Others: CO; HBr; SO_3		present	---	possible

** layer dependency

Why not test for mercury oxidation in a full bench reactor?



Test methods to measure mercury species

continuous

Different apparatus

- **wet chemical methods**
- **with converters**
- **using gold traps**

+ records peaks directly

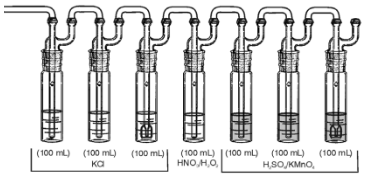
+ shows trending

- often inapplicable for low concentrations

- often cross sensitivity to other gas components

discontinuous

Ontario Hydro ASTM D 6784-02



+ used and tested since 1994

- difficult to handle

Dowex – carbon trap method

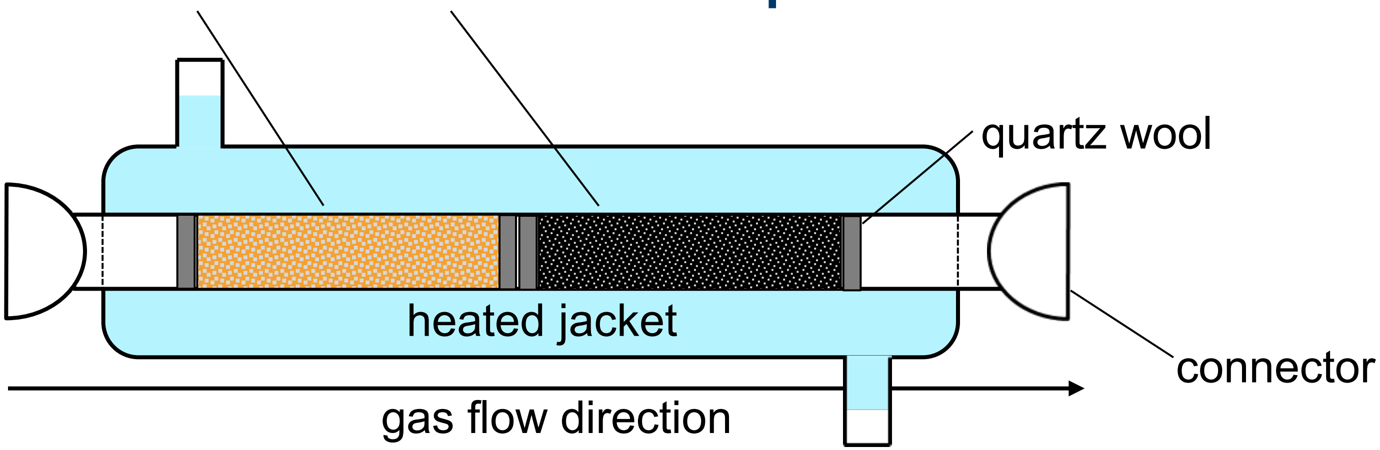
+ easier to use

+ well known in Europe

- not well established in US

Discontinuous mercury measurement

Dowex – activated carbon trap method



- Hg^{2+} adsorbs at Dowex (Styrene vinyl resin)
- Hg^{0} adsorbs at iodinated charcoal

→ separated analytic makes speciation of mercury possible

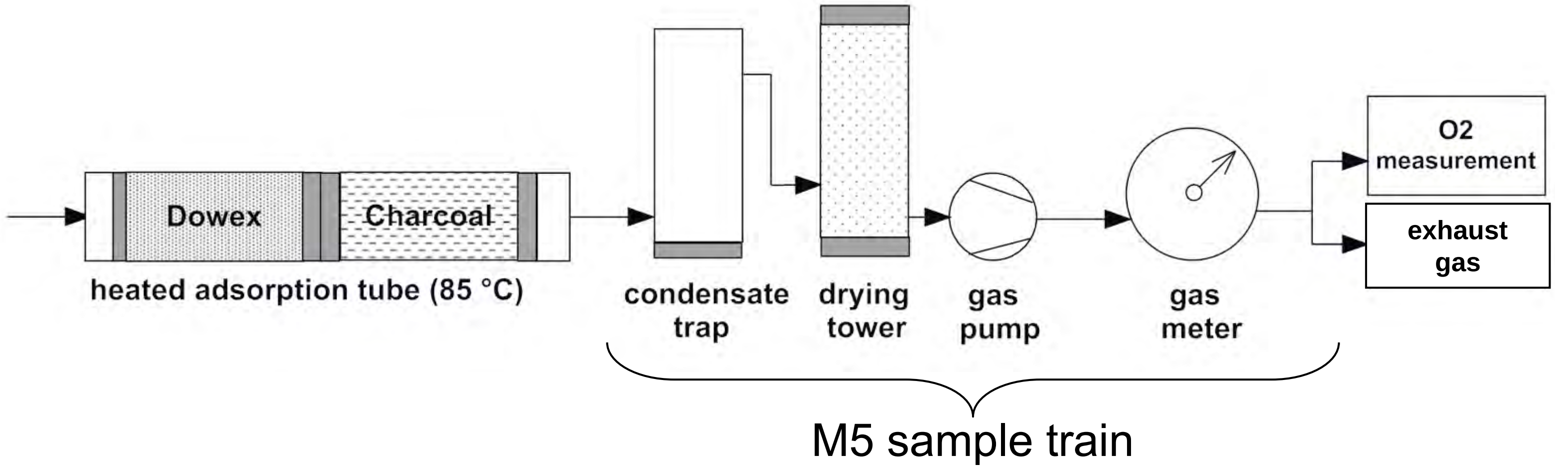
→ mercury oxidation over catalyst becomes documentable

Mercury species measurement

Dowex – activated carbon trap method

- gas sampling by pulling gas through adsorber tube (45 min)
- three sample trains: one at inlet and two at outlet of catalyst
- three sequential samplings per location and catalyst (3 x 45 min)

→ nine samples of Dowex (Hg^{2+}) and charcoal (Hg^{0}) to analyze on each test run (1 day)



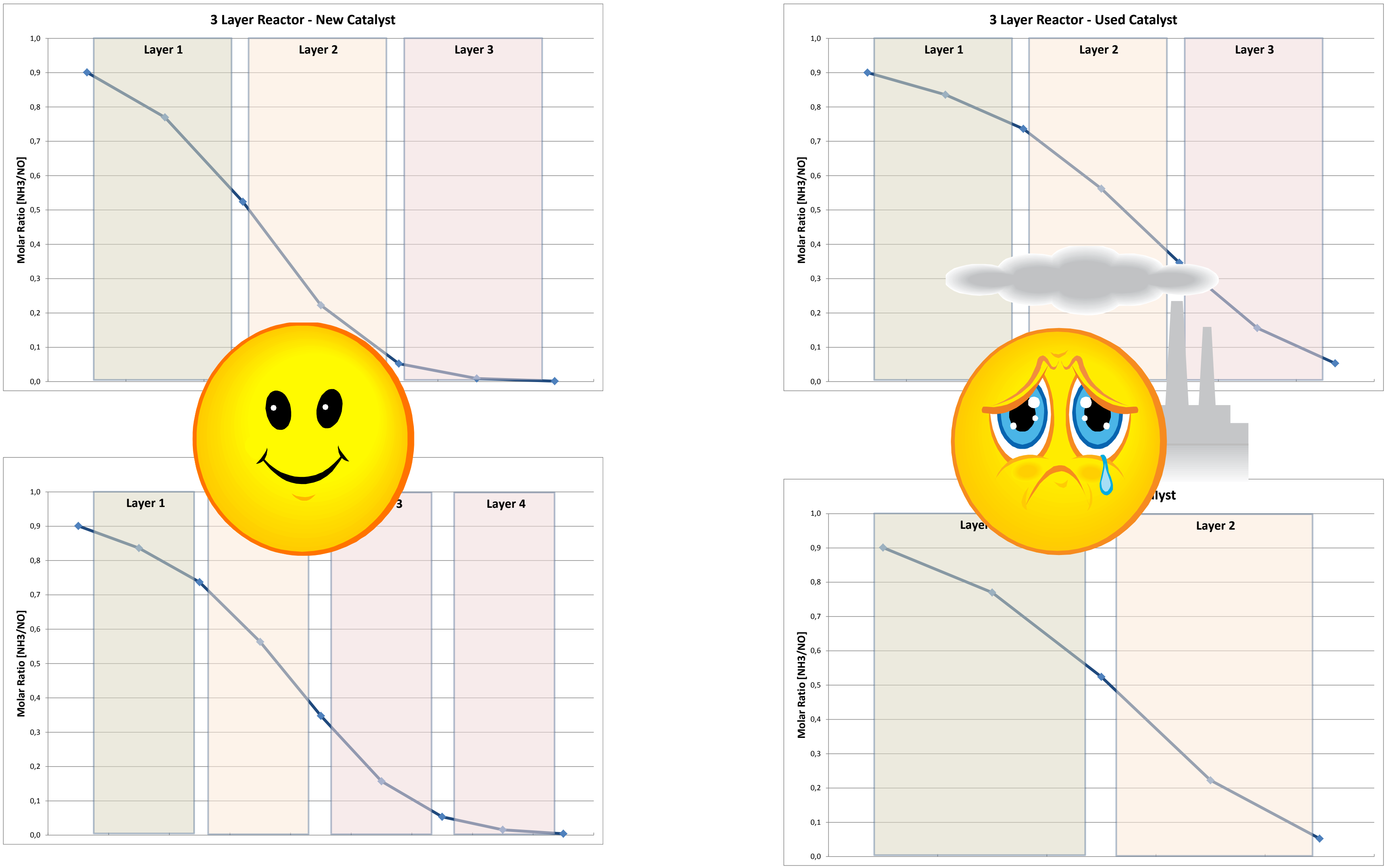
Sample analytics by Lumex RA 915$^+$

- thermic desorption of mercury in a heated camber (A)

- qualitative and quantitative measurement of mercury
  with Zeeman atomic absorption spectrometry

Detection limit 0.05 µg/m³ (minimum sampling of 1 m³)

Layer dependency NH_3 to NO ratio



Where do we stay?

We

- know mercury testing is very complex.
- know the basic factors like T, NH_3, flow, Cl, etc.
- know techniques to sample and analyze Hg^{2+} / Hg^0

  → but which one to prefer?
- can calculate Hg oxidation activity.
- know coal quality and composition influences Hg activity of catalysts.

- can not compare results of two labs.
- can not compare lab results with field performance.
- can not forecast the Hg performance for the next years.
- have no standard for testing Hg oxidation performance of catalysts.
- do not know, how different components of flue gas influence each other in their effect on Hg oxidation.

History of SCR Technology

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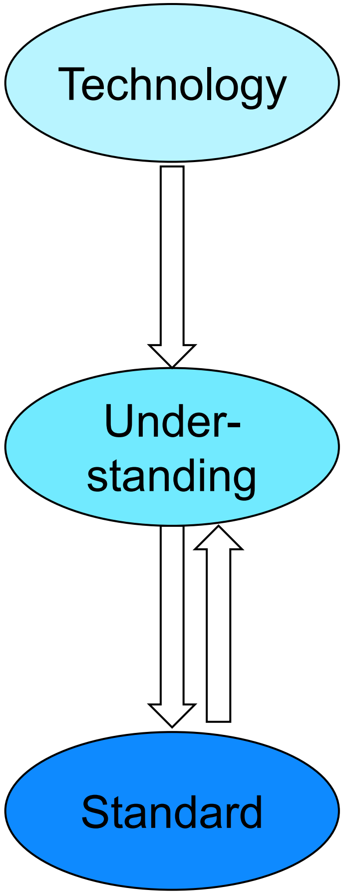

1970th	**Development of SCR technology in Japan**
1985	**First slip stream reactors in Germany**
End 80th	**first full size SCRs in Germany**
	Problem you can not compare activity from vendor A with vendor B (house methods)
	German power plant operator decide to establish a guideline for catalyst testing → VGB R302
1995	**2nd edition VGB guideline + Round Robin Test**
2007	**Epri guideline for catalyst testing**
2013	**3rd edition VGB guideline**

Current Status

We are currently in the same position with Hg testing as we were 30 years back with the SCR technology.

The next steps

- Continue Lab testing (Micro / Semi bench)
- Developing a standard guideline incl. methods to analyze Hg^0 / Hg^{2+}
- Round Robin tests
- Comparing Lab results with field performance
- Establishing of scale up/down factors
- Understanding of these factors
- Improve test protocol to minimize these factors

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