Mercury Sorption and Mercury Oxidation by Chlorine and Bromine at SCR DeNOx Catalyst
(Part A: Oxidation)

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Process development since 2000

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Cooperations in USA and Canada since 2005

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ALSTOM-Environmental Control Systems, Knoxville/TN, USA,
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Electric Power Research Institute, Palo Alto/CA, USA,
holding a research grant
for demonstration test runs

Southern Company Services, Inc.
Birmingham/AL, USA
Mass ratio for complete mercury bromination: \( \text{Br/Hg} = 100 \ldots 500 \) (“without SCR”)

In a case “with SCR” considerably smaller bromine demand about \( \text{Br/Hg} = 20 \ldots 50 \) only?
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   (Adsorptive competition between HX and Hg$^{\text{ox}}$, displacement of oxidised mercury by HX/X$_2$)
Up and Down Stream Sections of a SCR DeNOx catalyst bed

Low AV \([Nm^3/(m^2 \cdot hr) = m/hr]\) or corresponding low SV \([Nm^3/(m^3 \cdot hr) = 1/hr]\)

do elongate the extension of the HgOx-active part

DeNO\(_x\)-active part

NH\(_3\) is reducing Hg\(^{ox}\) and displacing Hg\(^{el}\)
in conjunction with NO, SO\(_2\),…
(chemically enhanced desorption of Hg\(^{el}\))
see e.g. Thorwarth et al.,
Clearwater Coal Conference (2005)

HgOx-active part

Hg\(^{el}\) and Hg\(^{ox}\) are adsorbed
HX/X\(_2\) is oxidizing Hg\(^{el}\) and displacing Hg\(^{ox}\)
(chemically enhanced desorption of Hg\(^{ox}\))
see e.g. Vosteen et al.,
VGBP\text{owerTech} (2003)
Stationary estate of the SCR DeNOx catalyst bed:

The mercury load \([\text{mg } \text{Hg}_{\text{total}}/\text{kg}]\) is constant

\(\rightarrow\) The mass fluxes of adsorbing and desorbing mercury are symmetrical and simultaneous (netto)

or (with other words)

Hg-adsorption and chemically enhanced Hg-desorption are in “dynamic equilibrium“

\[ \text{Hg}_{\text{total at SCR-entry}} = \text{Hg}_{\text{total at SCR-exit}} \]

„Mercury Oxidation Only (after break through)“

The sometimes open questions might be:
Changes in mercury speciation – caused by reactions or by displacement?
Instationary estate of SCR DeNOx catalyst bed:

The catalyst’s mercury load \([mg \text{ Hg}_{\text{total}}/kg]\) is increasing or decreasing all the time

\[\Rightarrow\] The mass fluxes of adsorbing and desorbing mercury are not symmetrical and not simultaneous

(ad-/desorption phenomena become visible by separation as in Gaschromatography)

Continuous spiking

Discontinuous spiking
Laboratory Research on mercury oxidation at SCR-DeNO$_x$ catalysts

commercial SCR-DeNO$_x$-catalysts

0 - 0,53 - 2,5 - 4,5 Ma.-% V$_2$O$_5$

0 - 2000 µg Hg/Nm$^3$

c. 15 g ... 31 g

4 x 4 channels
6,5 ... 13 cm long

2 x 0,5 g

crashed

Duration of laboratory test runs:

24 hours up to some days

Duration of laboratory test runs:

Some hours up to one day
Global reactions in Hg-Chlorination

\[
\begin{align*}
4 \text{HCl} + \text{O}_2 & \leftrightarrow 2 \text{H}_2\text{O} + 2 \text{Cl}_2 & \text{Chlorine-Deacon-Reaction} \\
\text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} & \leftrightarrow \text{SO}_3 + 2 \text{HCl} & \text{Chlorine-Griffin-Reaction} \\
\text{SO}_2 + \frac{1}{2} \text{O}_2 & \leftrightarrow \text{SO}_3 & \text{SO}_2/\text{SO}_3-Conversion \\
\text{Hg} + \text{Cl}_2 & \leftrightarrow \text{HgCl}_2 & \text{direct Hg-Chlorination} \\
\end{align*}
\]

„only direct mercury chlorination“

Working hypothesis for mercury oxidation at SCR catalyst (Vosteen):

Free chlorine relevant also for mercury chlorination at SCR catalyst

→ Catalysis of the Chlorine-Deacon Reaction to be studied
Global reactions in Hg-Bromination

\[
\begin{align*}
4 \text{HBr} + \text{O}_2 & \leftrightarrow 2 \text{H}_2\text{O} + 2 \text{Br}_2 & \text{Bromine-Deacon-Reaction} \\
\text{SO}_2 + \text{Br}_2 + \text{H}_2\text{O} & \leftrightarrow \text{SO}_3 + 2 \text{HBr} & \text{Bromine-Griffin-Reaction}\,* \\
\text{SO}_2 + \text{Br}_2 + 2 \text{H}_2\text{O} & \leftrightarrow \text{H}_2\text{SO}_4 + 2 \text{HBr} & \text{Bromine-Bunsen-Reaction}\,* \\
\text{SO}_2 + \frac{1}{2} \text{O}_2 & \leftrightarrow \text{SO}_3 & \text{SO}_2/\text{SO}_3-\text{Conversion} \\
\text{Hg} + \text{Br}_2 & \leftrightarrow \text{HgBr}_2 & \text{direct Hg-Bromination}
\end{align*}
\]

* in boiler temperature range thermodynamically not favoured

Working hypothesis (Vosteen):
Free bromine likewise crucial for mercury bromination at SCR catalyst

→ Catalysis of Bromine-Deacon Reaction to be studied
Test runs at a PC-fired wet bottom boiler (100 MW\textsubscript{therm})

Flue gas composition

- 98 mg Cl\textsubscript{total}/Nm\textsuperscript{3} dry
- 1039 mg SO\textsubscript{2}/Nm\textsuperscript{3} dry
- 29.8 g H\textsubscript{2}O/Nm\textsuperscript{3} dry
- 5.0 vol.-% dry

Hg\textsuperscript{el} / Hg\textsubscript{total}

Test runs at boiler unit N230 of BAYER AG in Uerdingen (Vosteen 1993)

Hg\textsuperscript{2+} / Hg\textsubscript{total}

High-Dust-SCR (Gutberlet 1992)

way through the boiler

Temperatures [°C]

modeling of mercury speciation at Boiler Unit N230 of BAYER AG

(Stop Temperature Method of Vosteen)
Catalysis of the Chlorine Deacon Reaction
(industrial research at a tail-end-SCR in 1997 and 1998 and laboratory research in 2002)

„Direct evidence for the Deacon reaction in SCR catalysts has not been given“

see
In Plant Research in 2000/2001

at Hazardous Waste Combustion Plants in Leverkusen, Dormagen and Uerdingen (Germany) of similar design with waste heat recovery boiler, multistage wet scrubber, wet ESP, tail-end SCR-DeNO₉.
controlled addition of sulphur granulat to kiln
Hg_{met} scrubbed gas and in front of SCR
[μg Hg / Nm^3 dry]

SO_2 boiler raw gas
[mg SO_2/Nm^3 dry]

Cl_{total} = ca. 20.000 mg/Nm^3 dry

Artificial oscillations of SO_2 are inducing concurrent oscillations of Hg_{met} at boiler exit because SO_2 is consuming Cl_2 in boiler raw gas

(Vosteen et al., Air Quality Conference (IV), Arlington, Washington D.C., 2003)
Lower SCR heat exchanger, PTFE

Upper SCR heat exchanger, steel
Total mass of catalyst: **19,242 kg** (two beds)

working temperature of 300 °C

gas residence time at 300 °C:
1 sec (half load)
or
0,5 sec (full load)

BASF Honeycomb SCR-catalyst (TiO₂, WO₃ and V₂O₅ as active component)
Chlorine Deacon-Reaction (equilibrium calculation for tail end SCR)

Reconversion of Cl₂ back to HCl:
If Cl₂ were passing the HWCI scrubber, reconversion back to HCl should happen.

Temperature [°C]

Cl₂- and HCl-equilibrium concentration [mg/Nm³ dry]

Scrubbed HWCI flue gas in front of tail end SCR

- vO₂ = 11 vol.-% dry
- vH₂O = 25 vol.-% dry
- pₐₕₑₛ = 1000 mbar
- cCl₂total = 100 mg/Nm³
- cSO₂ = 25 mg/Nm³

Θₕₐ₅₀/₅₀% = 120 °C
Retro-Chlorine Deacon Reaction catalysed in an industrial tail end SCR
(20 tons of catalysts – Vosteen, 1997)
Retro - Chlorine Deacon Reaction catalysed in an industrial tail end SCR
(20 tons of catalysts – Vosteen, Hübner 1998)
Chlorine-Deacon (laboratory test in humid air, Sandra Straube, July 2002)

The difference between the calculated conversion rates (thermodynamical equilibrium) and the measured conversion rates is growing with decreasing temperature (making kinetical limitations visible).

10.000 mg Cl\text{total}/Nm^2 dry

humid air

\(v_{O2} = 21\ \text{vol.-% dry}\)

\(v_{H2O} = 15\ \text{vol.-% dry}\)

\(p_{total} = 1000\ \text{mbar}\)
Chlorine:
Equivalence Temperature << SCR-Temperature

\( \Theta_{50/50\%} \) [°C]

- high-dust-SCR
- tail-end-SCR

HCl-concentration [mg/Nm\(^2\) dry]

\( \Theta_{50/50\%} \) << \( \Theta_{SCR} \) ⑧ mainly HCl
Catalysis of the Bromine Deacon Reaction and of the Iodine Deacon Reaction
(laboratory research in 2002)
Bromine:

Equivalence Temperature > SCR-Temperature

\[ \vartheta_{50/50\%} > \vartheta_{\text{SCR}} \]

\( \vartheta_{50/50\%} \) \text{ mainly Br}_2

(bromine radicals not considered)
Bromine Deacon (equilibrium calculation)

\[ \delta_{50/50\%} = 1100 \, ^\circ\text{C} \]

- \( v_O_2 = 11 \, \text{vol.-% dry} \)
- \( V_{H_2O} = 7.7 \, \text{vol.-% dry} \)
- \( p_{ges} = 1.000 \, \text{mbar} \)
- \( c_Br_{total} = 5.000 \, \text{mg/Nm}^3\,\text{dry} \)
HBr-Conversion [% of Br\textsubscript{total}] to Br\textsubscript{2} in humid air of 150 °C
(1.000 mg HBr/Nm\textsuperscript{3} dry, laboratory tests, Sandra Straube July 2002)
HI-Conversion [% of $I_{total}$] to $I_2$ in humid air of 150 °C

(1,000 mg HI/Nm$^3$ dry, laboratory tests, Sandra Straube July 2002)
4. Mercury oxidation by Chlorine and Bromine at SCR DeNOx catalyst

\textbf{Hg_{total}^- and Hg_{met}^- CEMs at the SCR measuring points 16, 18, 19, 20}

\textbf{Hg_{total}^- SCEM at the stack measuring point 17}
Artificial oscillations of SO$_2$ are inducing countercurrent oscillations of Hg$^{\text{ion}}$ at SCR exit because SO$_2$ is suppressing NaOCl in scrubber and therewith Cl$_2$ behind scrubber

(Vosteen et al., Air Quality Conference (IV), Arlington, Washington D.C., 2003)
Laboratory Research on mercury oxidation at SCR-DeNO$_x$ catalysts

commercial SCR-DeNO$_x$-catalysts

- 0 - 0,53 - 2,5 - 4,5 Ma.-% V$_2$O$_5$
- 0 - 2000 µg Hg/Nm$^3$

c. 15 g ... 31 g

4 x 4 channels 6,5
... 13 cm long

2 x 0,5 g

post graduate research by Dipl.-Ing. Sandra Straube
Honeycomb catalyst
4 x 4 canals, 12.5 cm long
2.5 weight-% V₂O₅, AV = 10 m/h

160 μg Hg^{el}/Nm³
5 mg/Nm³ HCl + SO₂

Laboratory tests with humid air, 160 μg Hg^{el}/Nm³ dry and 5 mg HCl/Nm³ added
(no NH₃ and no NOₓ)

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Influence of Cl₂ and SO₂ on mercury chlorination at SCR catalyst (not denox-active)
Influence of Br₂ on mercury bromination at SCR catalyst (not denox-active)

Laboratory tests with humid air, 160 µg Hg\textsuperscript{el}/Nm\textsuperscript{3} dry and **only 0.5 mg HBr/Nm\textsuperscript{3} added** (no NH\textsubscript{3} and no NO\textsubscript{x})

Dipl.-Ing. Sandra Straube, MLU Halle-Wittenberg

Honeycomb catalyst
4 x 4 canals, 12.5 cm long
2.5 weight-% V\textsubscript{2}O\textsubscript{5}, AV = 10 m/h

160 µg Hg\textsuperscript{el}/Nm\textsuperscript{3}?

0.5 mg/Nm\textsuperscript{3} HBr + SO\textsubscript{2}
Conclusions (1)

The technology of bromine enhanced mercury oxidation under US Patent No. 6,878,358 may be applied alone („without SCR“) or in conjunction with SCR and wet FGD („with SCR), diminishing the bromine demand towards only 20 ... 50 ppm bromide addition per coal.

Following the proposed modeling, mercury oxidation is proceeding as so-called direct halogenation by Cl$_2$ and/or Br$_2$ (or by the respective radicals) as well in boiler flue gases as at SCR catalysts. Main aspects of mercury chlorination and/or mercury bromination can be easily explained by the behaviour of the Chlorine Deacon Reaction and the Bromine Deacon Reaction respectively.

As demonstrated by industrial in-plant research and lately too by laboratory research, both reactions – providing the elementary mercury Hg$^{el}$ with Cl$_2$ or Br$_2$ as reaction partner – are catalysed at SCR DeNOx catalysts, shown at Honeycomb TiO$_2$, WO$_3$-catalysts with different contents of V$_2$O$_5$ as active component.

The Chlorine-Griffin-Reaction (re-consumption of Cl$_2$ by SO$_2$) is catalysed there too.
Conclusions (2)

The complex mechanism of mercury oxidation at SCR catalysts in coal combustion flue gases is interrelated with processes of adsorption and chemically enhanced desorption of both mercury species and of other chemical species (HCl, Cl₂ or HBr, Br₂, SO₂, SO₃ etc).

The sorption phenomena will be described in Part B.

Outlook

In summer 2006 a full scale demonstration of bromine enhanced mercury oxidation will be performed at a coal-fired 500 MWe-unit with SCR
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Thanks for Your attention