Mercury Retention in the Catalyst Bed of a Tail-End-SCR Downstream of the Wet Flue Gas Cleaning of a Hazardous Waste Incineration Plant

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R. Ullrich, WastePro Engineering Inc.
Agenda

• Introduction - CURRENTA HWC Plant with tail-end-SCR

• Sulphur Granulat Injection

• Continuous Mercury Spiking under High Chlorine Load

• Discontinuous Mercury Spiking under High Chlorine Load

• Hg Sorption Isotherm of Tail-End SCR Catalyst at 305 °C Operating Temperature

• Continuous Mercury Spiking under High Bromine Load

• Discontinuous Mercury Spiking under High Bromine Load

• In-plant Research on Dioxin and Furan De-Novo-Synthesis

• Practical Relevance

• Licensees in USA
Much of the story was already presented at

Advanced Tutorial at the
2006 International Conference on Incineration
& Thermal Treatment Technologies
Savannah/GA, May 15th, 2006

Prof. Dr.-Ing. Bernhard W. Vosteen,
Vosteen Consulting GmbH, Cologne (Germany)

"Bromine enhanced Mercury Abatement from Power Generation and Waste Combustion Flue Gases – Fundamentals of Mercury Oxidation by Chlorine and Bromine – Results of In-Plant Research and of Laboratory Research"

... somebody listening?
... speaking about Hazardous Waste Incineration

CURRENTA GmbH & Co. OHG, Germany
1st Successful Industrial Application in operation since 2001 (4 Units)

Hazardous Waste Combustion plants with 30,000...80,000 Nm³/h dry each, CURRENTA GmbH & Co OHG in Leverkusen, Dormagen and Uerdingen, Germany. Waste heat recovery boiler (5), multistage scrubber (6, 7, 8), wet ESP (9), DeNOx-SCR (11)

Injection ports 13, 14 and 15 for continuous or discontinuous Hg-spiking. Measuring ports 16 and 17 with CEMs, partially used for mercury speciation
Spiking Mercury

Continuously

Discontinuously

at top of after burning chamber
100 ... 20,000 μg/Nm³ dry

at bottom of after burning chamber
500,000 ... 80 Mio μg/Nm³ dry

„Hg-bombs“ -> „Hg-clouds“
Mobile $H_g_{\text{total}}$ and $H_g_{\text{met}}$ CEMs at points 16, 18, 19, 20

Installed $H_g_{\text{total}}$ SCEM at point 17 (stack)

Mobile CEMs for $H_g_{\text{total}}$ and $H_g_{\text{met}}$ (HM1400 wet of DURAG/Verewa) around and within tail-end SCR-DeNOx in June 2000
Lower SCR heat exchanger, PTFE  
Upper SCR heat exchanger, steel
BASF Honeycomb SCR-catalyst
(TiO₂, WO₃ and V₂O₅ as active components)

Total mass of catalyst: **19,242 kg** (2 catalyst beds)

working temperature: 300 °C

gas residence time at 300 °C:
1 sec (half load) ... 0.5 sec (full load)
Two Mobile CEMs for $H_{\text{g\_total}}$ and $H_{\text{g\_met}}$ (HM1400 wet of DURAG/Verewa) at SCR-DeNOx
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Figure 4a: Screw feeder for sulphur granulate addition into the rotary kiln
Sulphur Granulate Injection into Rotary Kiln to prevent Cl\textsubscript{2} Break Through

(„Sulphur-Dosing Ramp“, Vosteen 1997)
Control Circuit for Sulphur Granulate Injection into Rotary Kiln
to avoid Cl\textsubscript{2} break through („Sulphur-Dosing Ramp“, Vosteen 1997)
Figure 5: Artificially induced oscillations of the SO₂ concentration are inducing – without any delay – concurrent oscillations of the Hg_sub_met concentrations.
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Figure 7: $Hg_{\text{met}} / Hg_{\text{total}}$ species fraction in the crude gas at boiler exit
Figure 11: Mercury oxidation above baseline by chlorine and by bromine
Why Bromine instead of Chlorine?

„Hg not reacting with HX“

\[ \text{Hg} + 2 \text{HX} + 0.5 \text{O}_2 \rightarrow \text{HgX}_2 + \text{H}_2\text{O} \]

Slow reaction

„Hg reacting with X\(_2\) or related radicals“

\[ \text{Hg} + \text{X}_2 \rightarrow \text{HgX}_2 \]

Quick reaction

Much more Br\(_2\) than Cl\(_2\) formed
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Figure 8: Hg bomb peaks for verification of the Hg_{met} retention in the tail-end SCR
Hg-Adsorption Isobares of Hg\textsuperscript{el} and Hg\textsuperscript{ox} (HgCl\textsubscript{2}) at a SCR-catalyst

160 µg Hg/Nm\textsuperscript{3} dry, crashed catalyst with 2.5 weight-% V\textsubscript{2}O\textsubscript{5} in humid air, 15 vol.-% H\textsubscript{2}O

Evaluation based on the different slopes:

Heats of adsorption in humid air

17 kJ/mol Hg\textsubscript{ion} (as HgCl\textsubscript{2})

61 kJ/mol Hg\textsubscript{met}

Adsorption Isobares of HgCl\textsubscript{2} and Hg\textsubscript{el} at a SCR-DeNO\textsubscript{x} Catalyst
(S. Straube et al., Applied Catalysis B: Environmental, 2008)
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high $Hg_{\text{total}}$ in the flue gas (9600 µg Hg/Nm$^2$ dry)

Figure 12: Mass ratio Br/Hg and achieved Hg removal rate in a test run spiking the boiler raw gas with 9,600 µg Hg$_{\text{total}}$/dscm
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- Appendix
Table 1: Injection of Hg bombs [g]

<table>
<thead>
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<th>Time</th>
<th>Hg</th>
<th>Time</th>
<th>Hg</th>
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<td>5</td>
<td>10:32</td>
<td>180</td>
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<td>10</td>
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<td>10:58</td>
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<tr>
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<tr>
<td>10:26</td>
<td>160</td>
<td>11:30</td>
<td>360</td>
</tr>
</tbody>
</table>

Experimental time [min]  Total Hg amount [g]

116  3400

Figure 13: Injection of larger and larger Hg-bombs (see Table 1) under sufficient bromine supply [6], [7]
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German Licensees of Vosteen Consulting

Town Karlsruhe – Wastewater Treatment Plant
2 Stationary Fluidized Bed Combustors
for Sewage Sludge
applying NaBr and PRAVO® since 2007
Martin Maurer, Roland Milz

EGLV – Central Sludge Treatment Plant Bottrop
2 Stationary Fluidized Bed Combustors
for Sewage Sludge
applying NaBr since 2004
Testing PRAVO® in 2004 and again in April 2008
Falko Lehrmann, Günter Schwabe
Wastewater Treatment Plant Bottrop and Central Sludge Treatment Plant Bottrop
Polychlorinated Dioxins (PCDD/F) as well as
Polybrominated Dioxins (PBDD/F)

analysed w/o and with bromine injection (diluted NaBr) into Fluidized Bed Combustor for Sewage Sludge for Mercury Control (Boiler, ESP, 2-stage WFGD):

PCDD/F = 1 ... 3 pg TEQ/dscm
<< 0.1 ng TEQ /dscm

PBDD/F = 0.3 pg TEQ/dscm

(detection limit 0.2 pg/dscm)
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HSE MSWC Darmstadt
3 units (220 t waste/year)
Testings (2 months)
Spiking Hg, NaBr, PRAVO™
3 + 1 SCEM (Mercem)

WFGD-tower with 2 stages (design: von Roll)
Figure 15: Example of a typical long time mercury elution peak from a tail-End SCR behind the wet scrubbing system of a municipal solid waste incinerator [9]
PRAVO™ container (diluted 1:10) for continuous addition to upper WFGD-stage

PRAVO™ (diluted 1:10) for discontinuous addition to upper WFGD-stage
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**KNX™ Coal Additives and Systems** as trademark of ALSTOM Power Inc.

Michael J. Rini, John Buschmann, Leif Lindau

Electric Power Research Institute, Palo Alto/CA, USA, research grant for demonstration test runs e.g. at the sites Monticello, Plant Miller

George Offen, Ramsay Chang

Southern Company Services, Inc. Birmingham/AL, USA, specific licensee for SC Utilities only

Larry Monroe, Mark Berry et. al.
Bromine enhanced mercury abatement, invented by Prof. Vosteen in 2000

German Patent DE 10 233 173
granted 2005

US Patent 6 878 358
granted 2005

Canadian Patent 2 435 474
granted 2006

European Patent 1 386 655
granted 2008

Australian Patent 2 003 220 713
granted 2008

Patent applications pending in other countries
Thanks for Your attention

Questions?