VOSTEEN Consulting GmbH

Thermal Engineering and Environmental Protection

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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International Conference on
Thermal Treatment Techologies (IT3)
May 12 - 16, 2008
Montreal, Quebec, Canada
Paper # 109

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
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- 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)

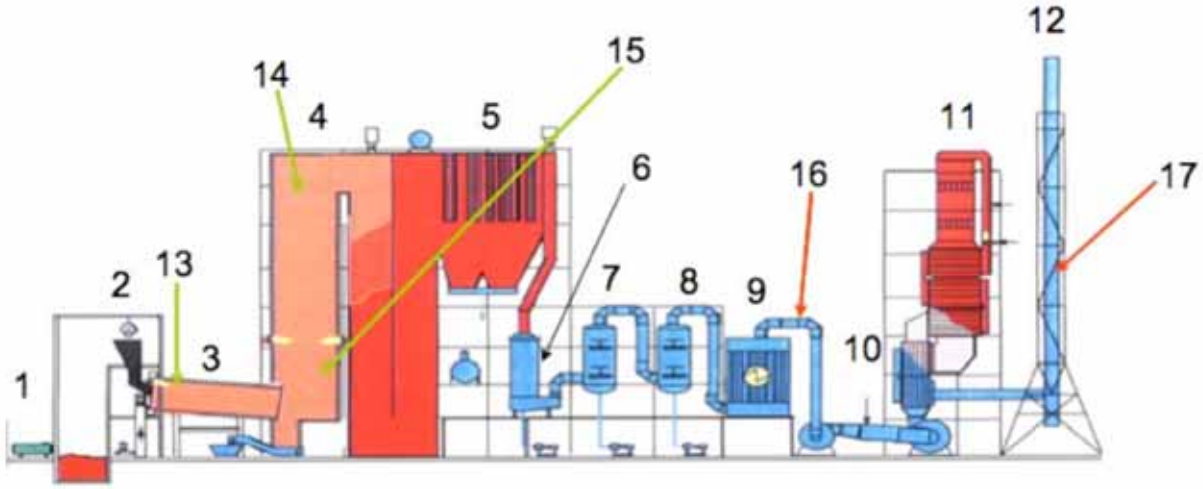
"Bromine enhanced Mercury Abatement from Power Generation and Waste Combustion Flue Gases – Fundamentals of Mercury Oxidation by Chlorine and Bromine – Results of In-Plant Research and of Laboratory Research"

... somebody listening?

... speaking about Hazardous Waste Incineration

CURRENTA GmbH & Co. OHG, Germany

1st Successful Industrial Application in operation since 2001 (4 Units)

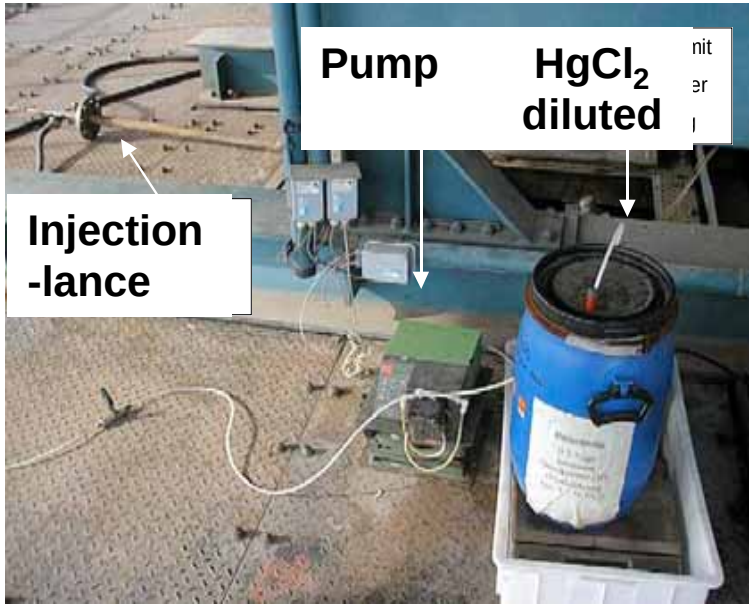


Hazardous Waste Combustion plants with 30,000. .. 80,000 Nm³/h dry each, CURRENTA GmbH & Co OHG in Leverkusen, Dormagen and Uerdingen, Germany. Waste heat recovery boiler (5), multistage scrubber (6, 7, 8), wet ESP (9), DeNOx-SCR (11)

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



at top of after burning chamber

100 ... 20,000 µg/Nm³ dry

Discontinuously

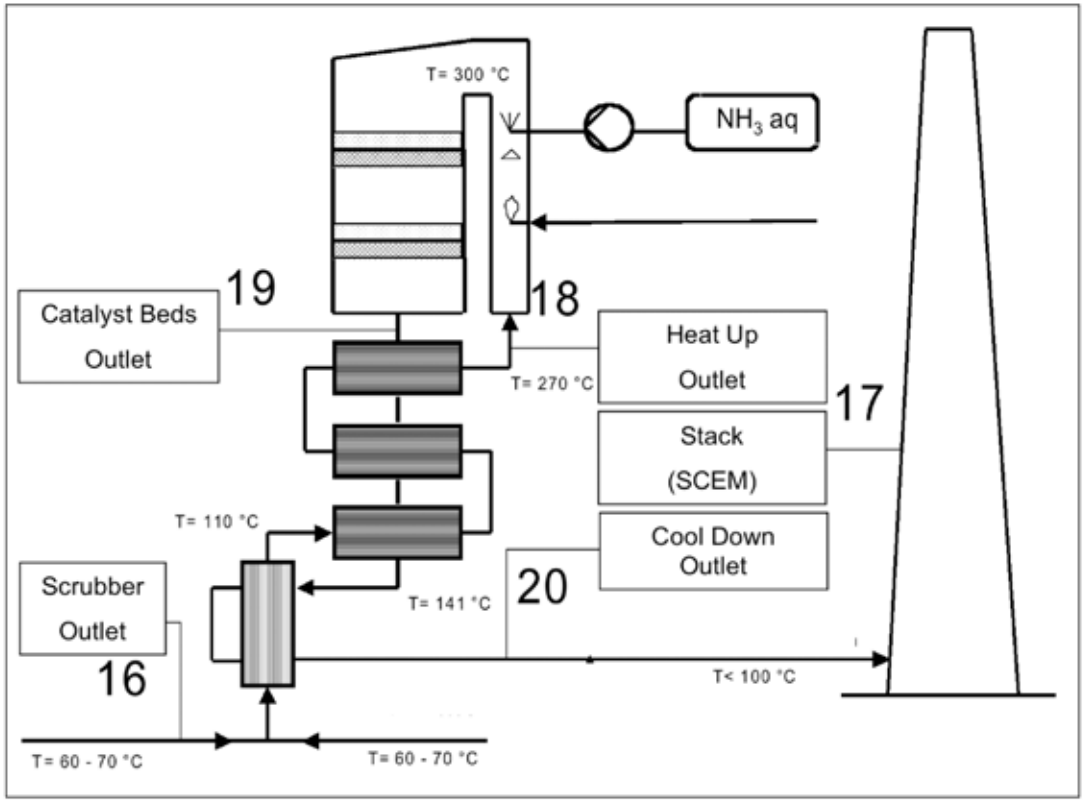
at bottom of after burning chamber

500,000 ... 80 Mio µg/Nm³ dry

„Hg-bombs“ -> „Hg-clouds“

Mobile Hg_{total} and Hg_{met} CEMs at points 16, 18, 19, 20

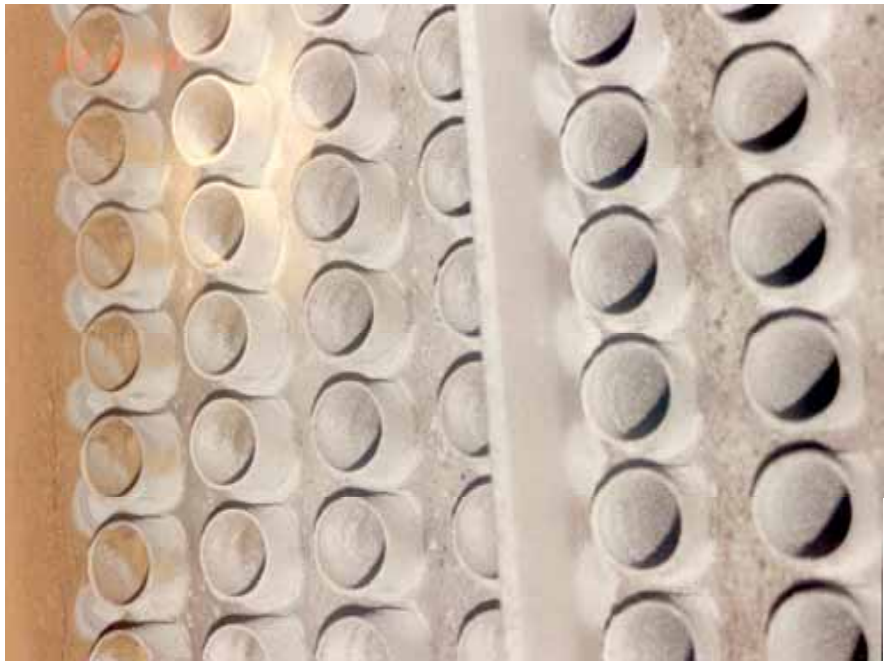
Installed Hg_{total}- SCEM at point 17 (stack)



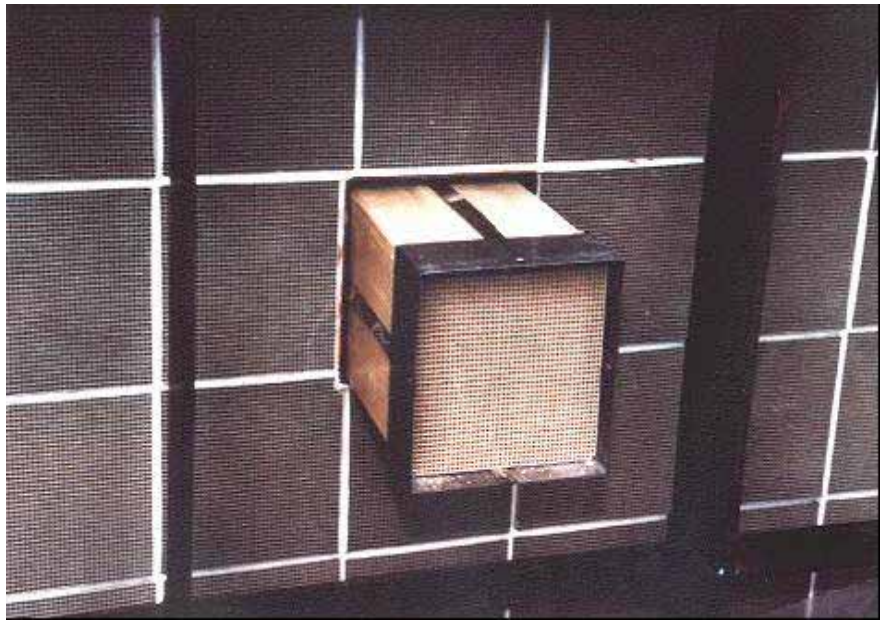
Mobile CEMsfor Hg_{total} and Hg_{met} (HM1400 wet of DURAG/Verewa)

around and within tail-end SCR-DeNOx in June 2000

Lower SCR heat exchanger, PTFE



Upper SCR heat exchanger, steel



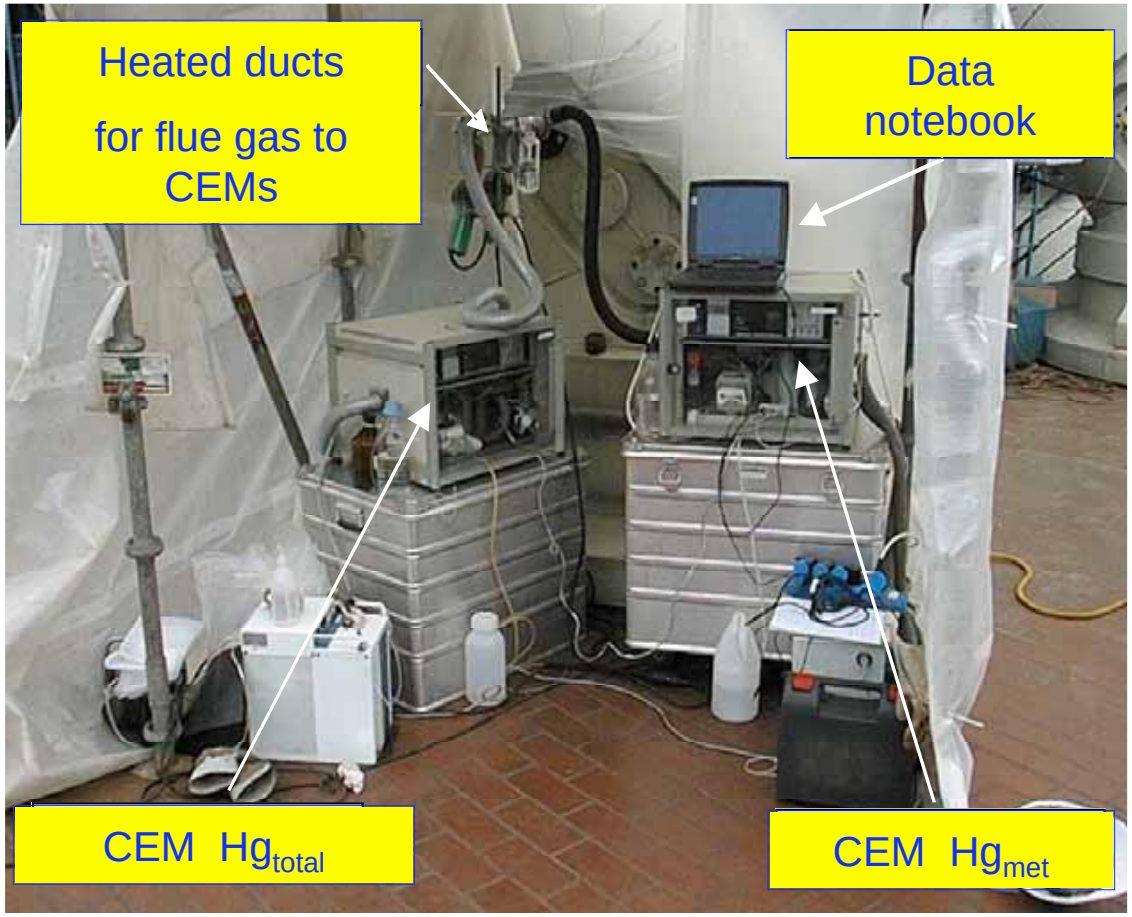
Total mass of catalyst: **19,242 kg** (2 catalyst beds)

working temperature: 300 °C

gas residence time at 300 °C:

1 sec (half load) ... 0,5 sec (full load)

BASF Honeycomb SCR-catalyst
(TiO_2, WO_3 and V_2O_5 as active components)



Two Mobile CEMsfor Hg_{total} and Hg_{met} (HM1400 wet of DURAG/Verewa) at at SCR-DeNOx

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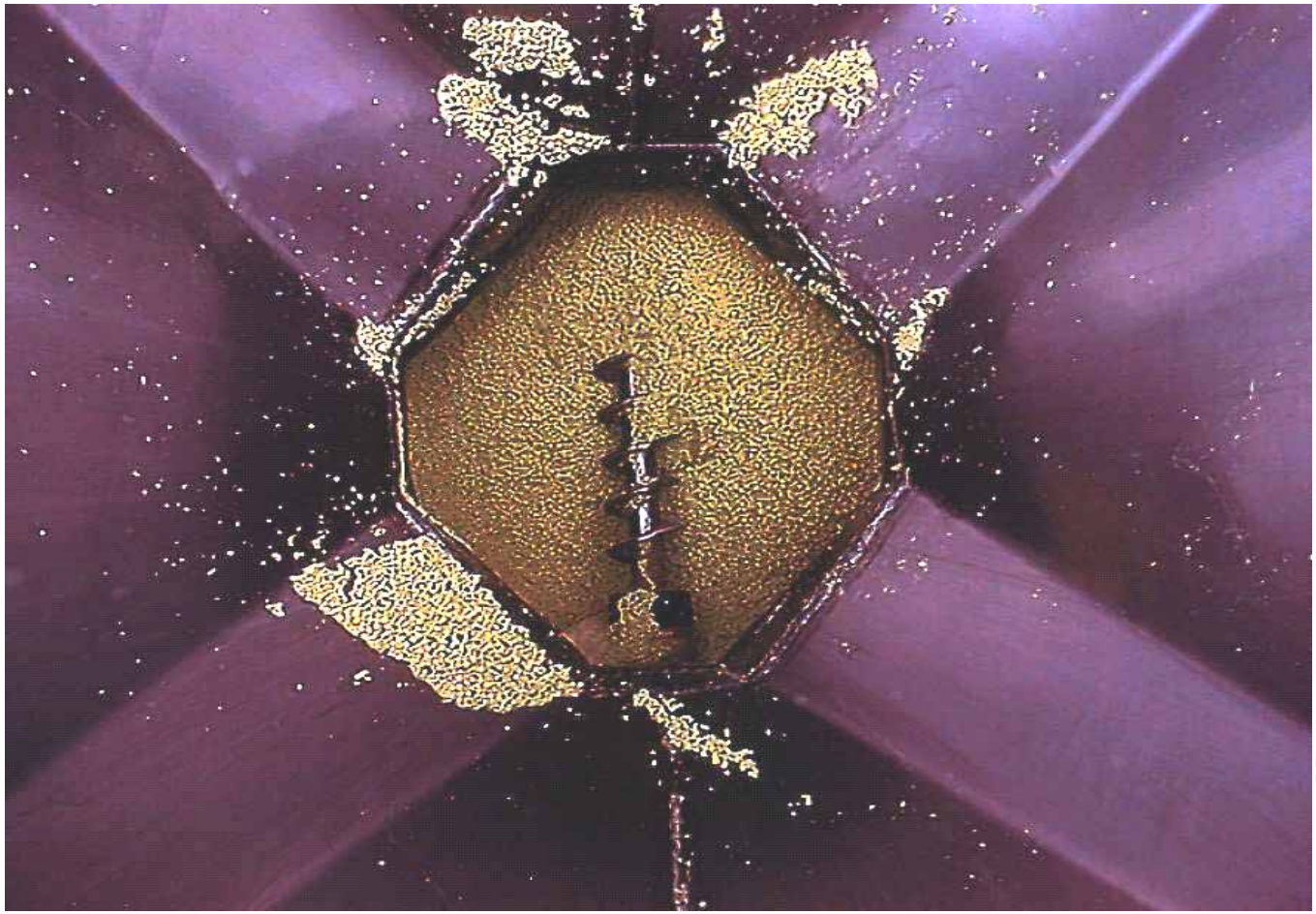
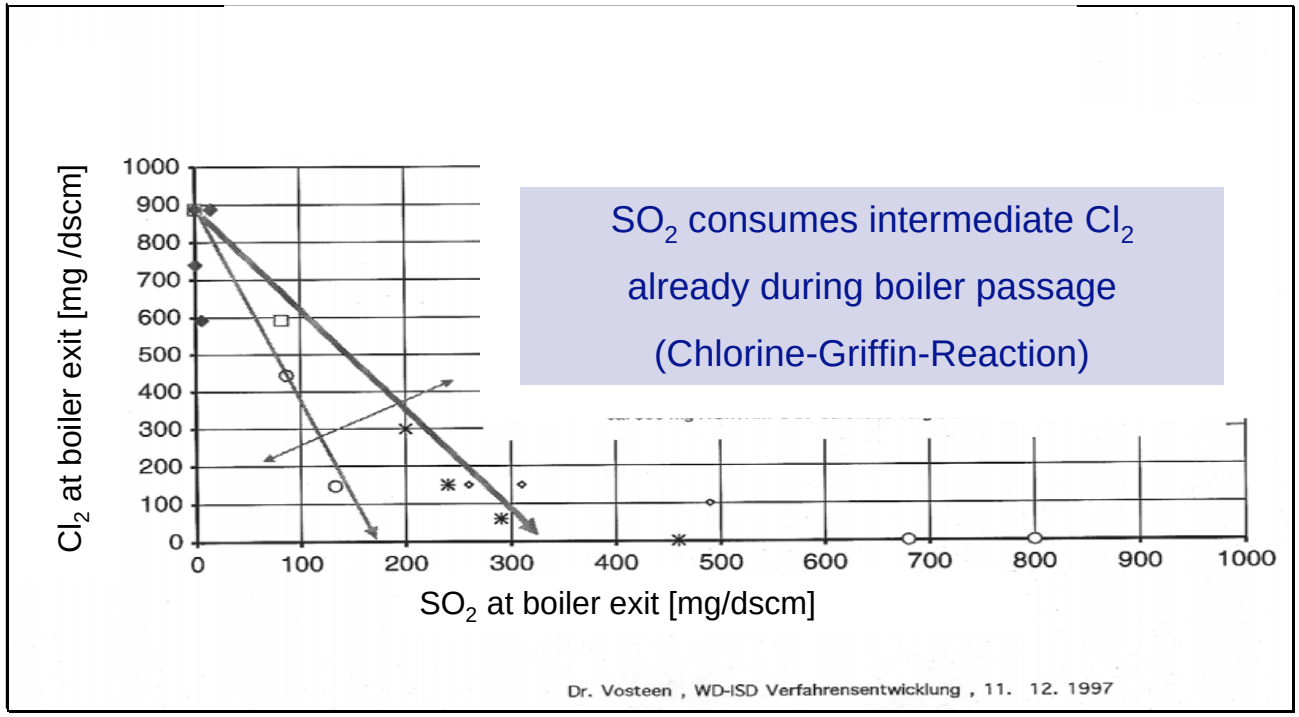
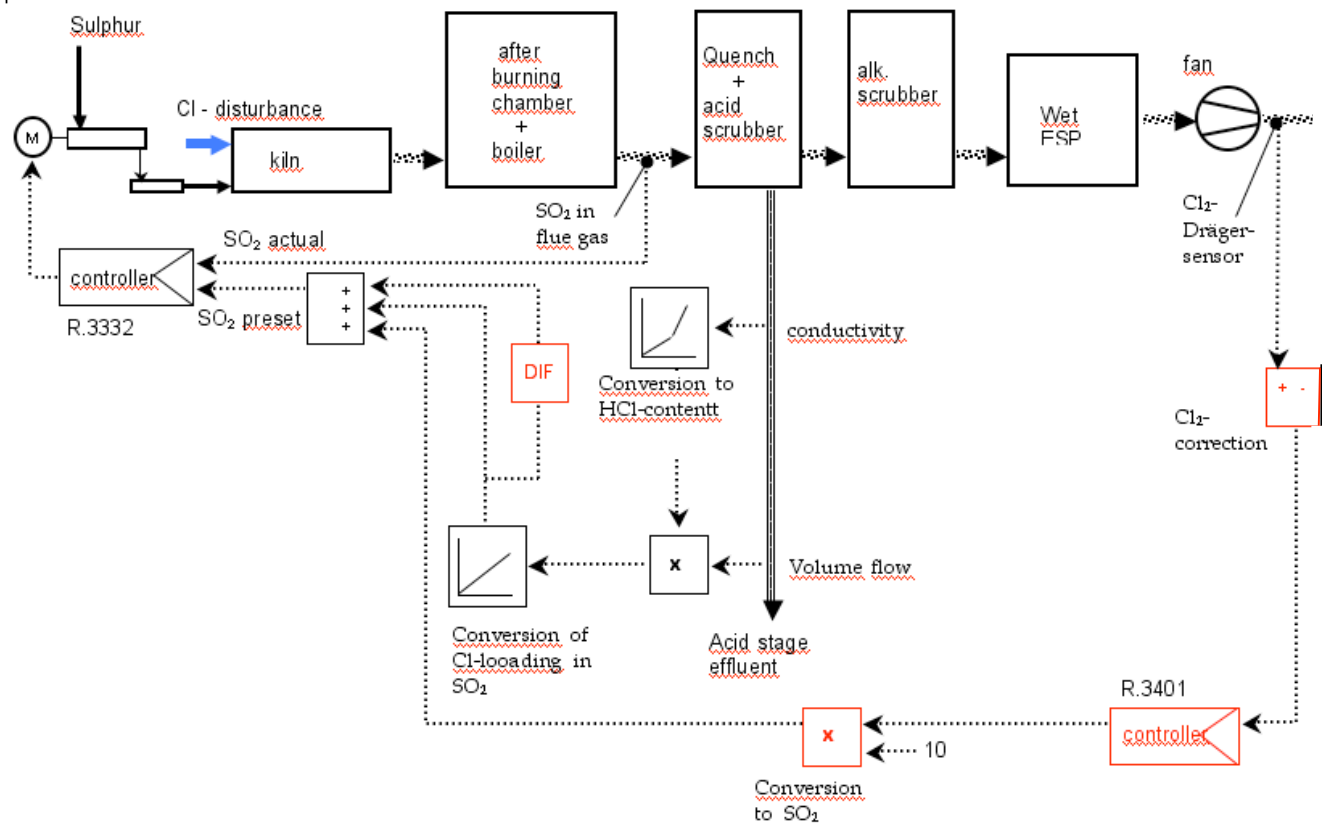


Figure 4a: Screw feeder for sulphur granulate addition into the rotary kiln



Sulphur Granulate Injection into Rotary Kiln to prevent Cl_2 Break Through

(„Sulphur-Dosing Ramp“, Vosteen 1997)



Control Circuit for Sulphur Granulate Injection into Rotary Kiln

to avoid Cl_2 break through („Sulphur-Dosing Ramp“, Vosteen 1997)

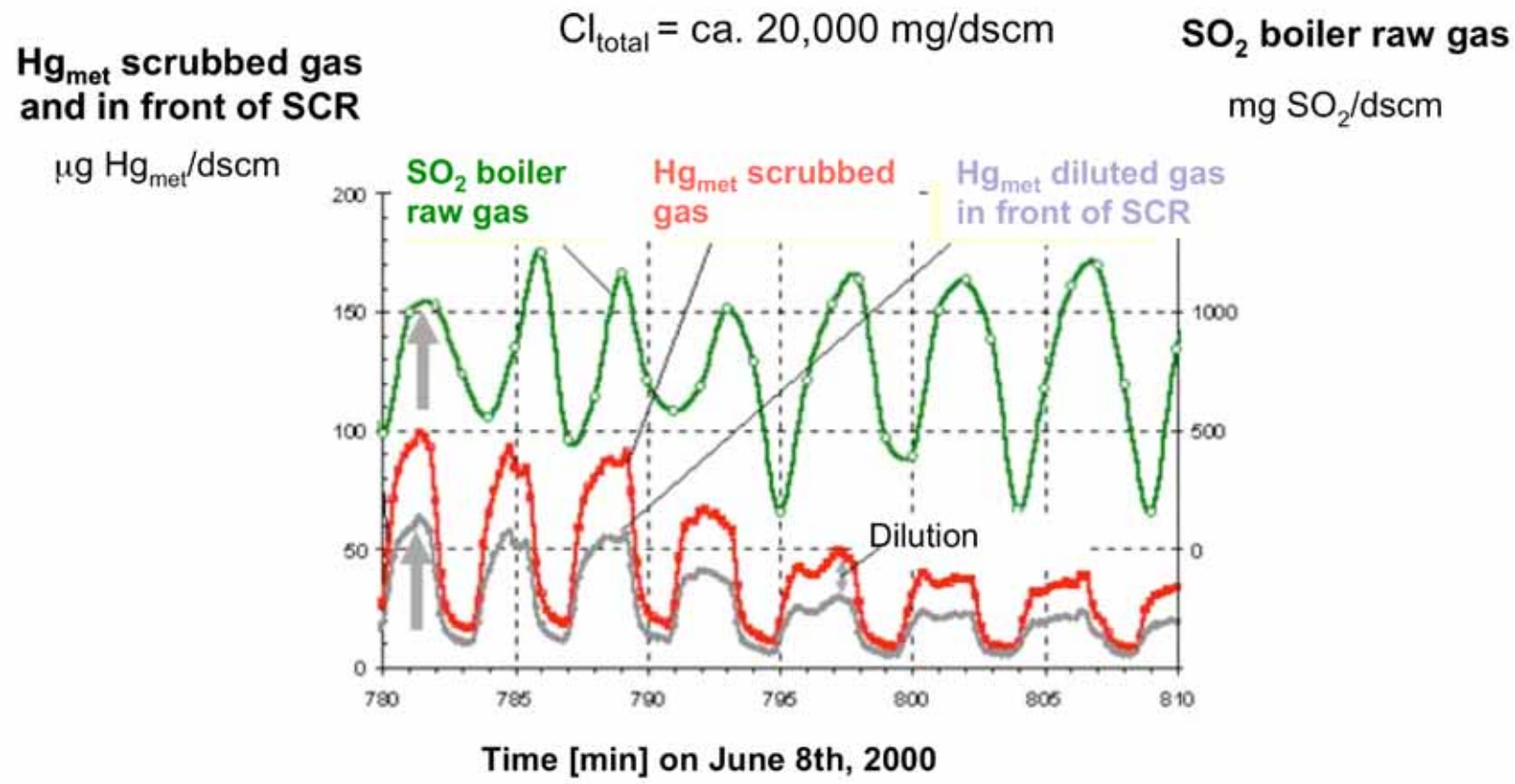


Figure 5: Artificially induced oscillations of the SO_2 concentration are inducing – without any delay – concurrent oscillations of the Hg_{met} concentrations

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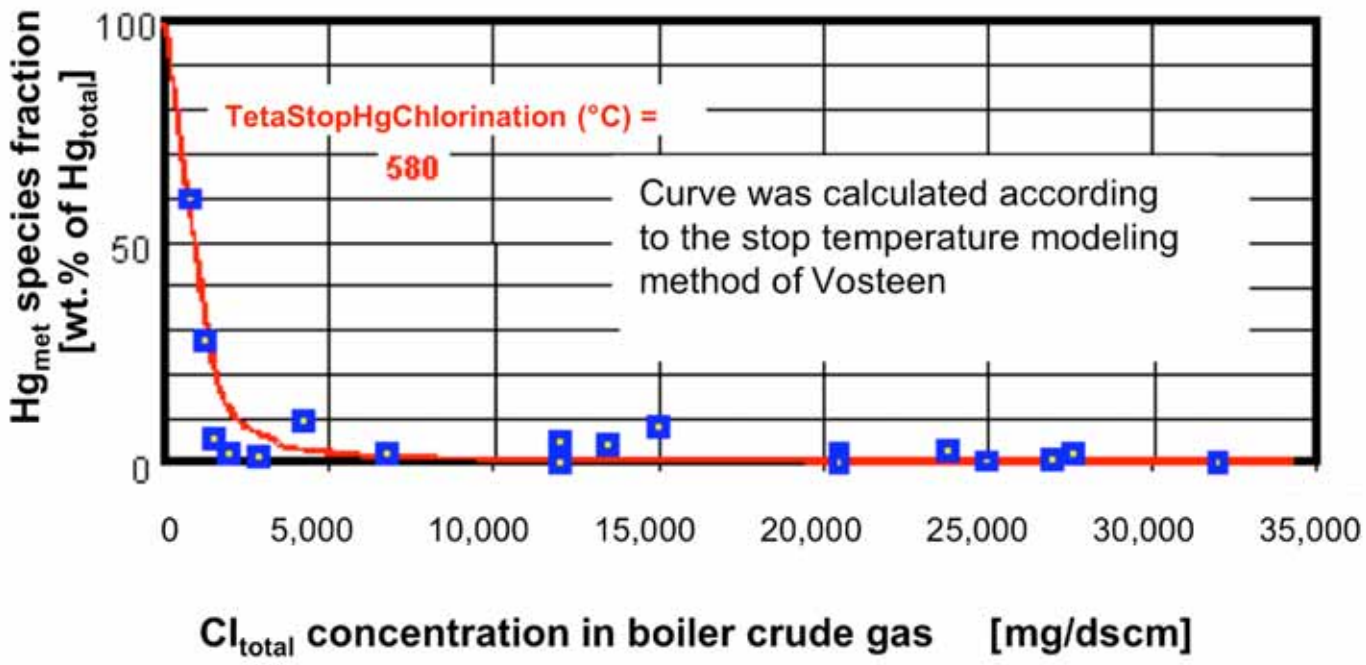

Figure 7: Hg_{met} / Hg_{total} species fraction in the crude gas at boiler exit

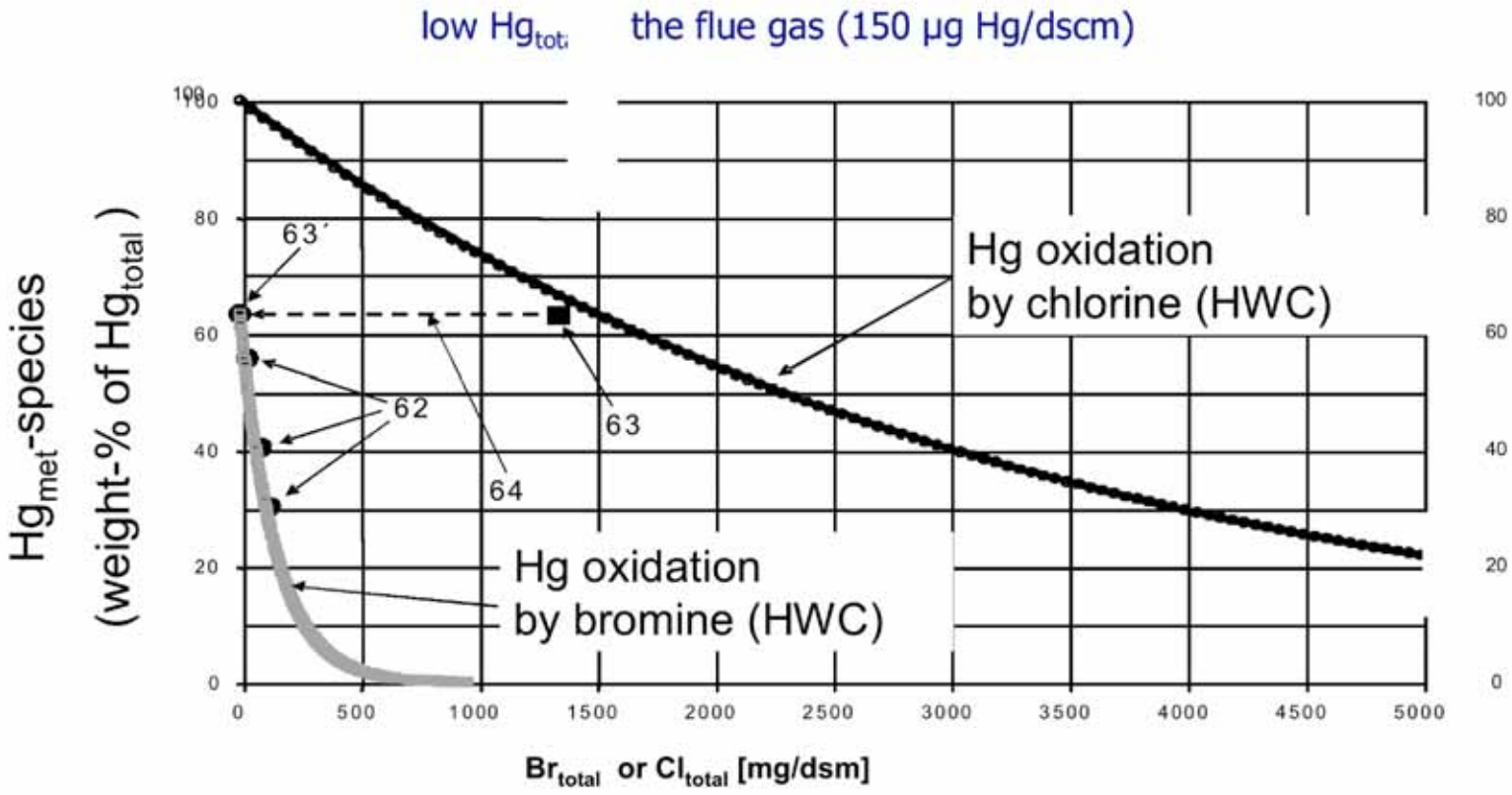

Figure 11: Mercury oxidation above baseline by chlorine and by bromine

Why Bromine instead of Chlorine?

„Hg not reacting with HX“

$Hg + 2\ HX + 0.5\ O_2 \rightarrow HgX_2 + H_2O$

Slow reaction

„Hg reacting with X_2 or related radicals“

$Hg + X_2 \rightarrow HgX_2$

Quick reaction

Much more Br_2 than Cl_2 formed

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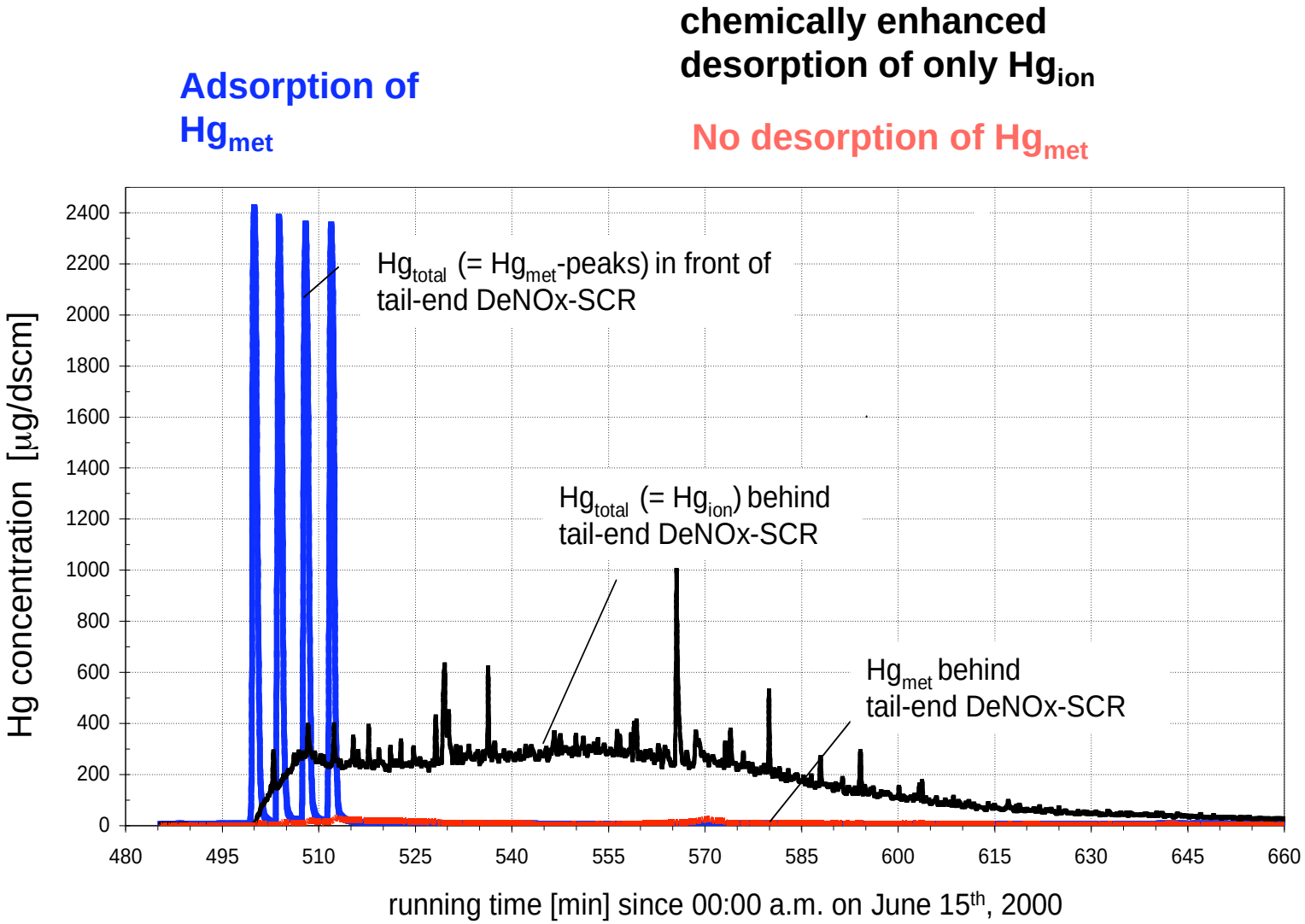
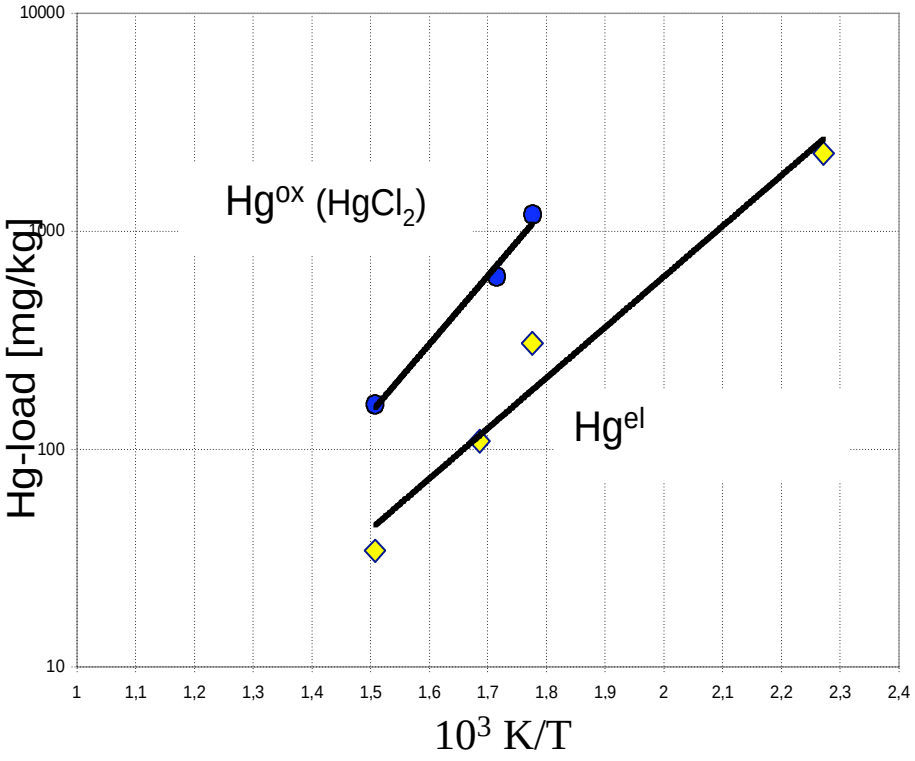


Figure 8: Hg bomb peaks for verification of the Hg_{met} retention in the tail-end SCR

Hg-Adsorption Isobares of Hg^{el} and Hg^{ox} ($HgCl_2$) at a SCR-catalyst

160 µg Hg/Nm³ dry, crashed catalyst with 2.5 weight-% V_2O_5 in humid air, 15 vol.-% H_2O



evaluation based on the different slopes:

Heats of adsorption in humid air

17 kJ/mol Hg_{ion} (as $HgCl_2$)

61 kJ/mol Hg_{met}

Adsorption Isobares of $HgCl_2$ and Hg_{el} at a SCR-DeNOx Catalyst
(S. Straube et al., Applied Catalysis B: Environmental , 2008)

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high Hg_{total} in the flue gas (9600 µg Hg/Nm? dry)

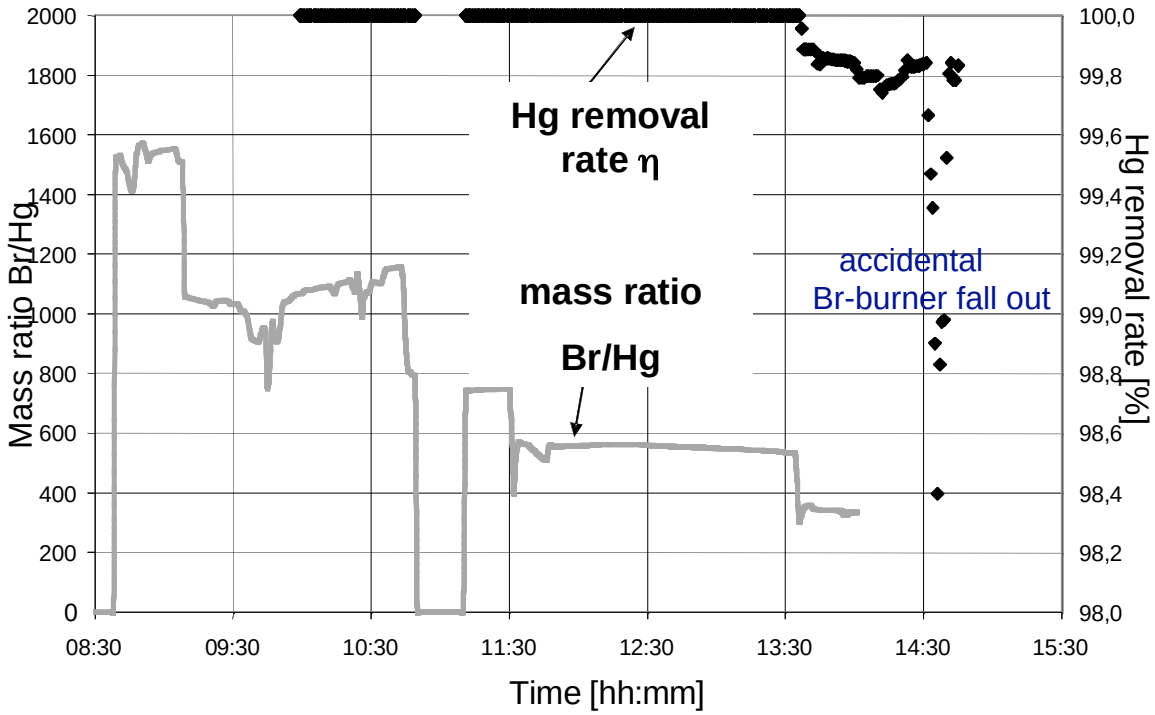

Figure 12: Mass ratio Br/Hg and achieved Hg removal rate in a test run spiking the boiler raw gas with 9,600 µg Hg_{total}/dscm

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- Appendix

Table 1: Injection of Hg bombs [g]

Time	Hg	Time	Hg
9:24	5	10:32	180
9:32	10	10:37	200
9:38	15	10:43	220
9:49	20	10:48	240
9:54	40	10:53	260
9:59	60	10:58	280
10:04	80	11:03	300
10:09	100	11:08	310
10:15	120	11:13	320
10:20	140	11:20	340
10:26	160		
Experimental time [min]		**Total Hg amount [g]**	
116		**3400**	

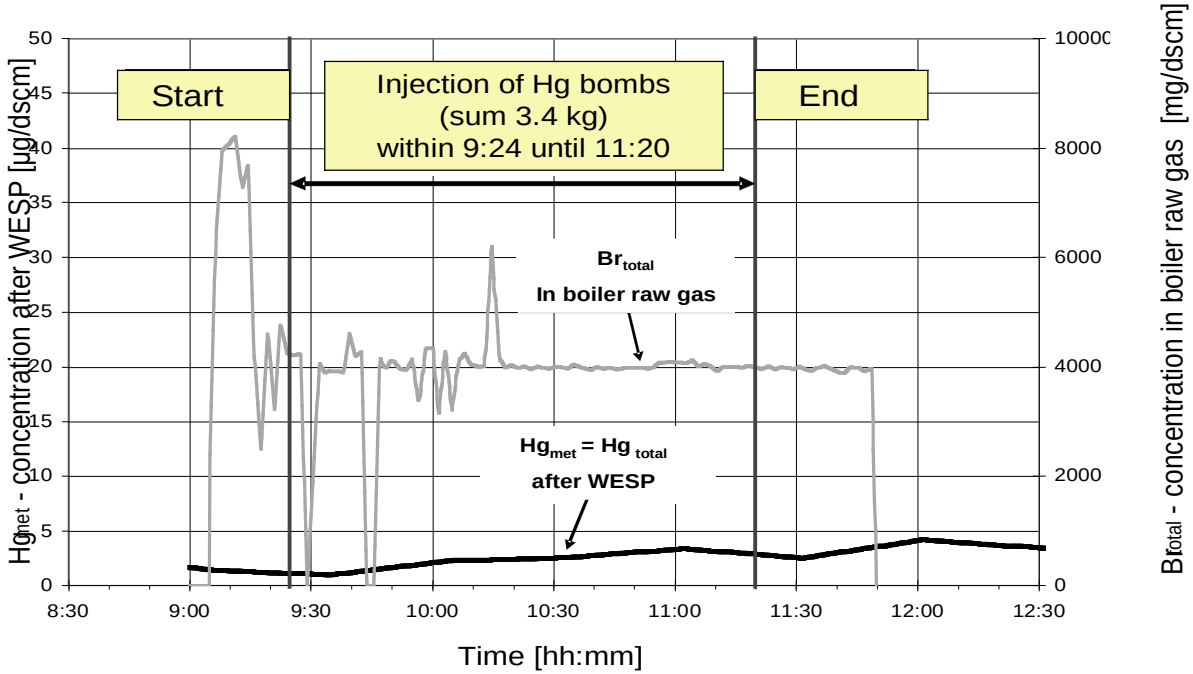

Figure 13: Injection of larger and larger Hg-bombs (see Table 1) under sufficient bromine supply [6], [7]

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German Licensees of Vosteen Consulting

Karlsruhe

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

EMSCHER GENOSSENSCHAFT
LIPPE VERBAND

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 Crontrol (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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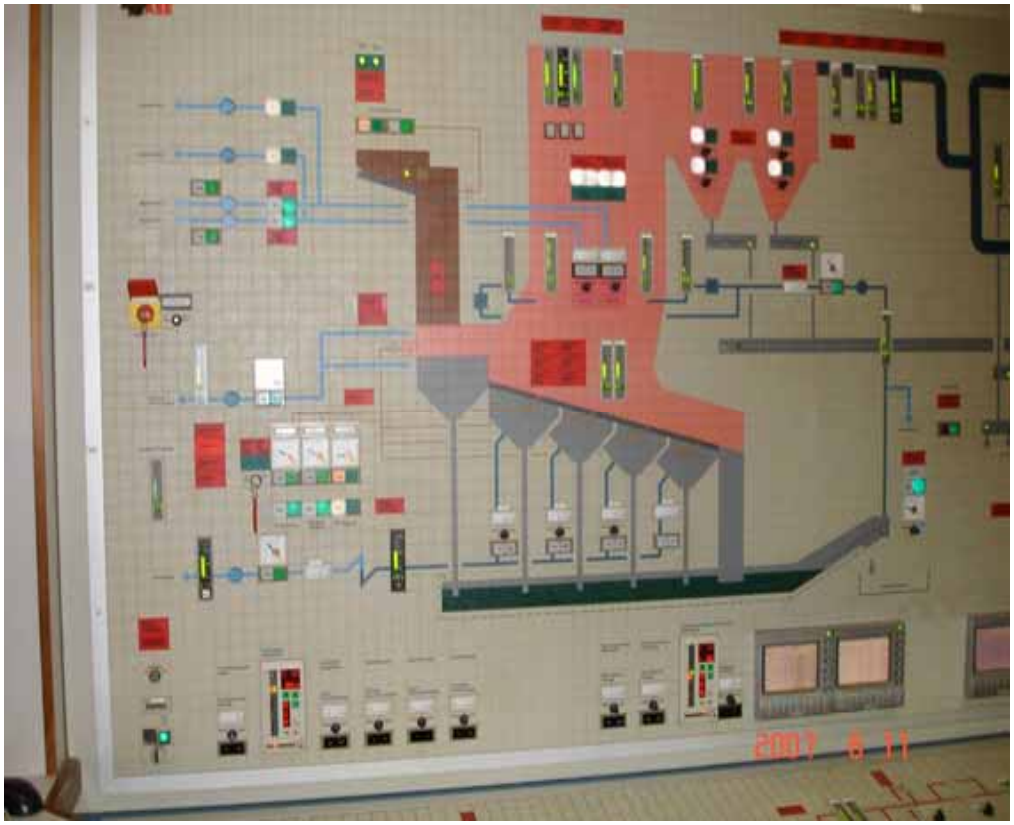
HSE
Energie für die Region

HSE MSWC Darmstadt

3 units (220 t waste/year)

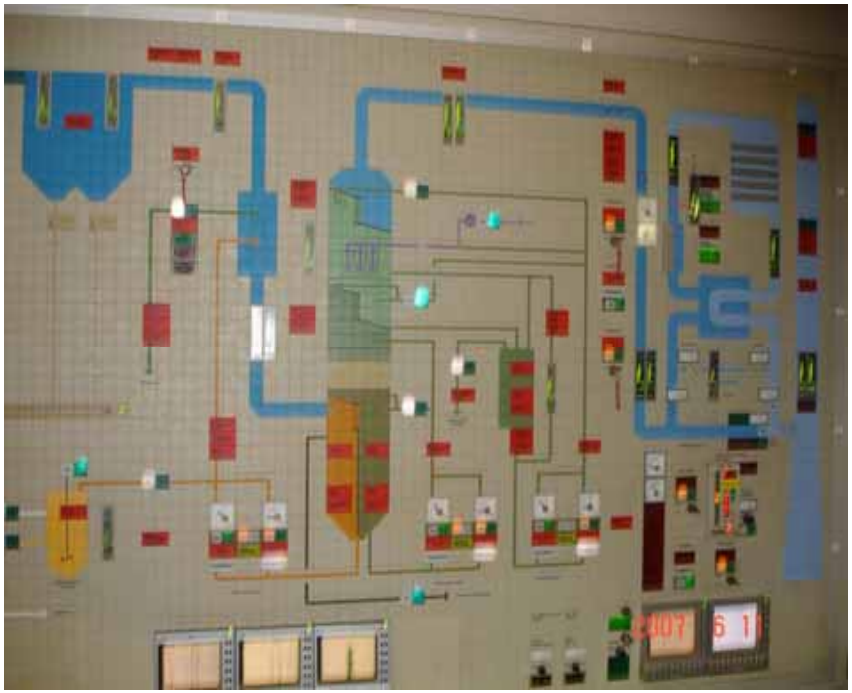


HSE
Energie für die Region

Testings (2 months)

Spiking Hg, NaBr, PRAVO™

3 + 1 SCEM (Mercem)



WFGD-tower with 2 stages (design: von Roll)

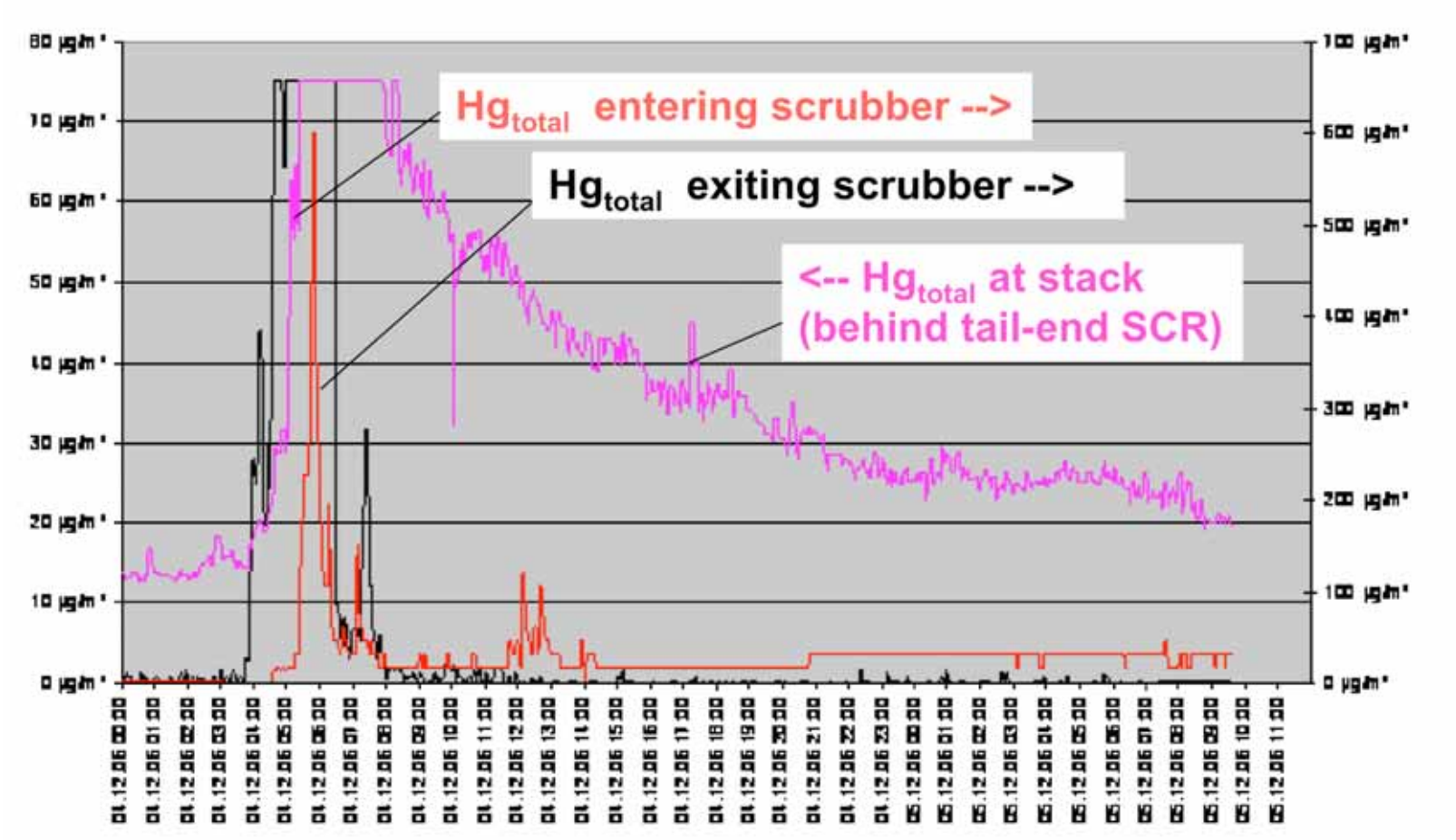


Figure 15: Example of a typical long time mercury elution peak from a tail-End SCR behind the wet scrubbing system of a municipal solid waste incinerator [9]

HSE
Energie für die Region

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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US Licensees of Vosteen Consulting

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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

US006878358B2

(12) **United States Patent**
Vosteen et al.

(10) **Patent No.: US 6,878,358 B2**
(45) **Date of Patent: Apr. 12, 2005**

(54) **PROCESS FOR REMOVING MERCURY FROM FLUE GASES**

(75) Inventors: **Bernhard Vosteen**, Cologne (DE); **Joachim Beyer**, Kuerten (DE); **Theodore-Gerhard Bonkhofer**, Essen (DE); **Olaf Fleth**, Grevenbroich (DE); **Andrea Wieland**, Maria Rojach (AT); **Andreas Pohontsch**, Goerlitz (DE); **Rico Kanefke**, Merseburg (DE); **Ewa Standau**, Merseburg (DE); **Claus Mueller**, Kuerten (DE); **Michael Nolte**, Goslar (DE); **Heinz Koeser**, Ingelheim (DE)

(73) Assignee: **Bayer Aktiengesellschaft**, Leverkusen (DE)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 24 days.

(21) Appl. No.: **10/430,088**

(22) Filed: **May 6, 2003**

(65) **Prior Publication Data**

US 2004/0086439 A1 May 6, 2004

Related U.S. Application Data

(63) Continuation-in-part of application No. 10/202,571, filed on Jul. 24, 2002.

(30) **Foreign Application Priority Data**

Jul. 22, 2002 (DE) 102 33 173

(51) **Int. Cl.**[7] **B01D 53/00**; C22B 43/00

(52) **U.S. Cl.** **423/210**; 75/670; 75/742

(58) **Field of Search** 423/210; 75/670, 75/742

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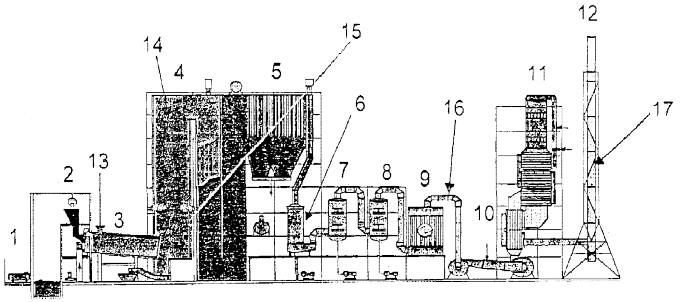
* cited by examiner

Primary Examiner—Stanely S. Silverman
Assistant Examiner—Jonas N. Strickland
(74) *Attorney, Agent, or Firm*—Norris McLaughlin & Marcus PA

(57) **ABSTRACT**

Process for removing mercury from flue gases of high-temperature plants, in particular power stations and waste incineration plants in which a bromine compound is fed to the multistage furnace and/or the flue gas in a plant section downstream of the furnace, the temperature during contact of the bromine compound with the flue gas being at least 500° C., preferably at least 800° C. The combustion is carried out in the presence of a sulphur compound, in particular sulphur dioxide. Subsequently to the furnace, the flue gas is subjected to an optional multistage cleanup for removing mercury from the flue gas, which cleanup comprises a wet scrubber and/or a dry cleanup.

16 Claims, 9 Drawing Sheets



Thanks for Your attention

Questions?