Reinhold Environmental Ltd.

2008 NOx-Combustion Round Table & Expo Presentation

February 4-5, 2008 in Richmond, VA

VOSTEEN Consulting GmbH

Thermal Engineering and Environmental Protection

Scale Up of Bromine Based Mercury Oxidation in Coal Combustion and Waste Incineration (Part B)

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Rico Kanefke, Currenta

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Cologne, Germany
phone: + 49 221 680 098 22

Reinhold Environmental
NOx-Combustion Round Table

Richmond VA, Thursday, February 5th, 2008

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In the following, further two parts of this workshop:

What we are mainly speaking about?

Some drops of BRAVO to the coal
(Bromine Additive Vosteen)

+

Some drops of PRAVO to the WFGD
(Precipitation Agent Vosteen)

might solve your mercury problem

in the most cost competitive way

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Bayer Industry Services

Bayer Industry Services GmbH & Co. OHG (Leverkusen, GER)

Currenta GmbH & Co OHG
former BAYER Industry Services
4 Rotary Kiln Incinerators
for Hazardous Wastes
Joachim Beyer, Theodor Bonkhofer, Rico Kanefke

VOSTEEN CONSULTING GMBH
Thermal Engineering and Environmental Protection

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Bromine enhanced mercury abatement Invented by Prof. Vosteen in 2001

German Patent DE 10 233 173
granted 2005

US Patent 6 878 358 *)
granted 2005

Canadian Patent 2 435 474 *)
granted 2006

European Patent 2 435 474
granted 2008

*) actual owner: Vosteen Consulting GmbH

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

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,238,488	A *	8/1993	Wilhelm	75/742
5,900,042	A *	5/1999	Mendelsohn et al.	75/742
2002/0114749	A1	8/2002	Cole	
2002/0114750	A1	8/2002	Holste et al.	

FOREIGN PATENT DOCUMENTS

CA	2150529	12/1995	
DE	42 18 672 C1	8/1993	F23G/7/00
DE	44 22 661 A1	1/1996	B01D/53/34
DE	19850054 A1 *	5/2000	B01D/53/77
EP	0 208 036 B1	10/1989	B01D/53/34
EP	0 709 128 A2	5/1996	B01D/53/94
JP	02000197811 A *	7/2000	B01D/53/64

OTHER PUBLICATIONS

Shoichi, Takao et al; 2000197811 A; Patent Abstracts of Japan; Jul. 18, 2000.

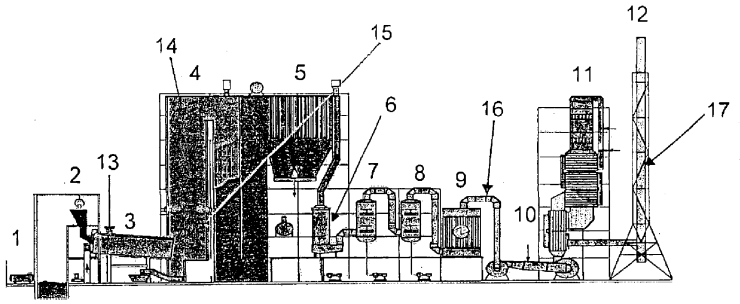
* cited by examiner

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



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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

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US Licensees of Vosteen Consulting

ALSTOM-Environmental Control Systems, Knoxville/TN, USA,
exclusive licensee for North America
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, Nick Irvin

URS

Carl Richardson

Katherine Dombrowski

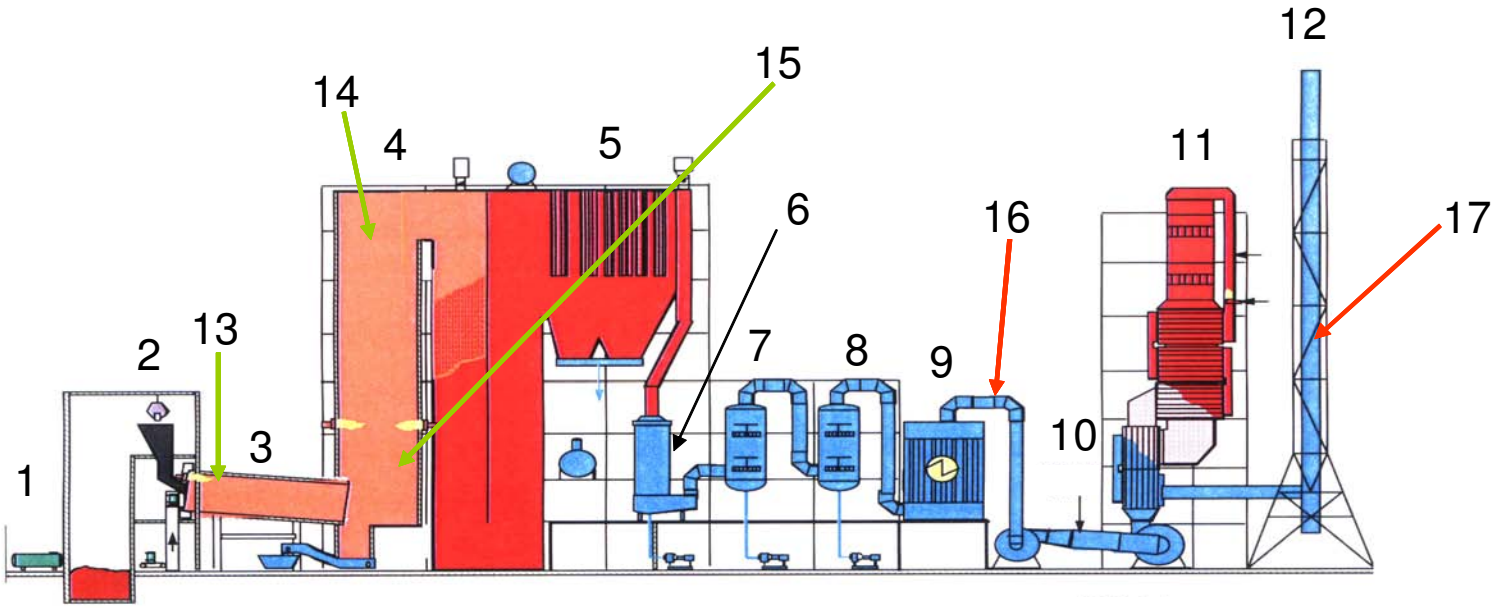
Jennifer Paradise

Gary Blythe

John Currie

et al.

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-spikin
Measuring ports 16 and 17 with CEMs, partially used for mercury speciation

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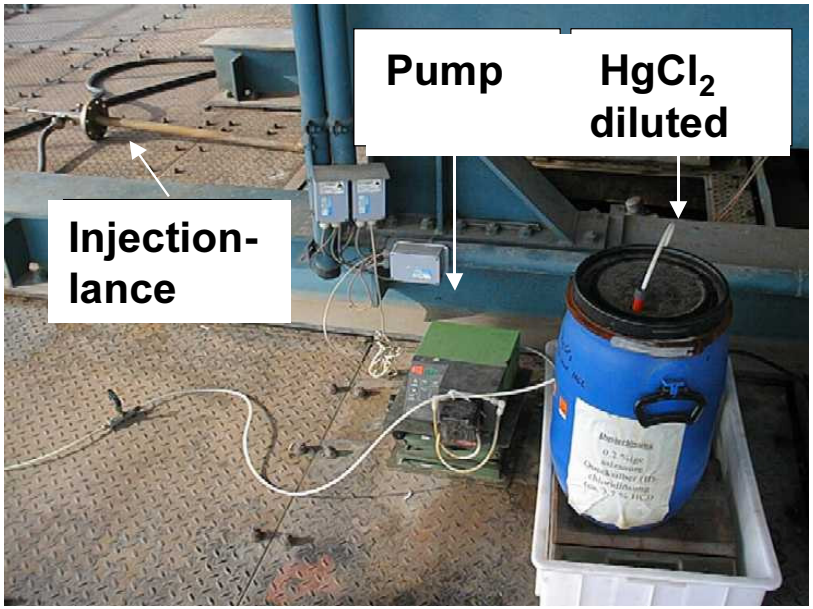
Hg-Spiking

Continuously



at top of after burning chamber

100 … 10,000 … 20,000 µg/Nm³ dry

Discontinuously

at bottom of after burning chamber

500,000 … 80 Mio µg/Nm³ dry

„Hg-bombs" ---> „Hg-clouds"

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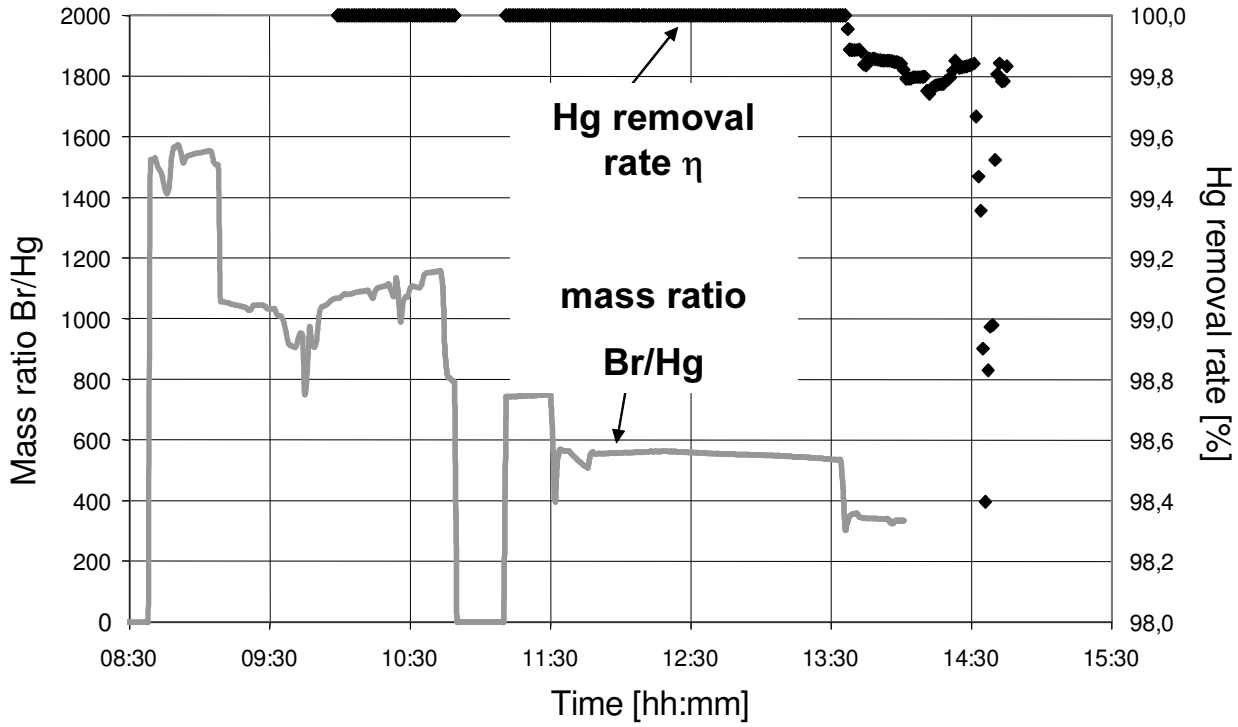
diploma thesis of Rico Kanefke, 2001,

high Hg_{total} in the flue gas (9600 µg Hg/Nm³ dry)



Mass ratio for complete mercury removal:

Br/Hg = 500 (“without SCR”)

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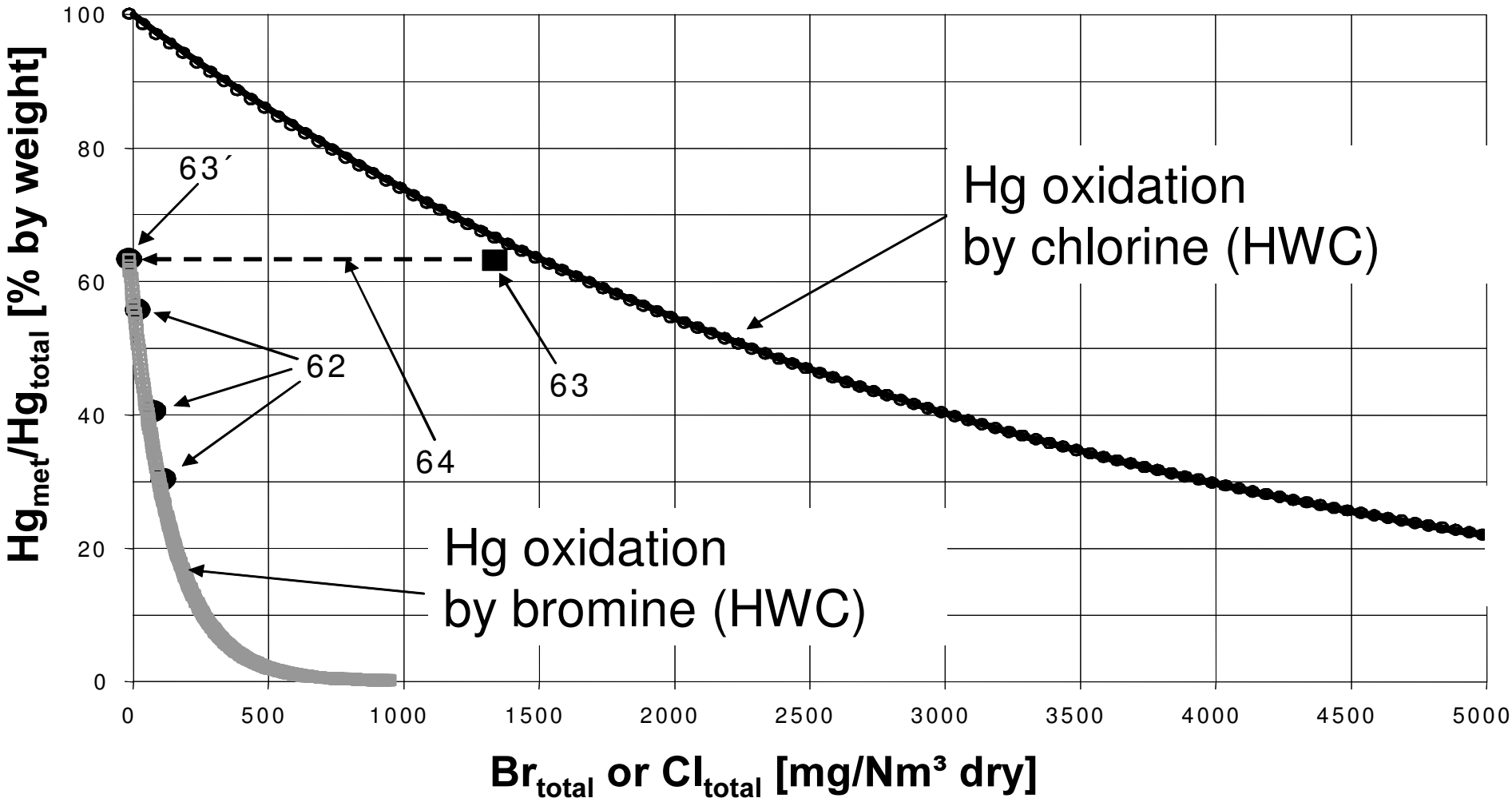
low Hg_{total} in the flue gas (150 µg Hg/Nm³ dry)



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Why Bromine instead of Chlorine?

Working hypothesis

„Hg not reacting with HX“

$Hg + 2\ HX + 0.5\ O_2 \rightarrow HgX_2 + H_2O$
is a too slow rection

„Hg reacting with X_2 or related radicals“

$Hg + X_2 \rightarrow HgX_2$
is a quick enough reaction

There is much more Br_2 than Cl_2 formed

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Chlorine Enhanced Hg-Oxidation

Relevant global reactions

$4\ HCl + O_2 \leftrightarrow 2\ H_2O + 2\ Cl_2$	Chlorine-Deacon-Reaction
$SO_2 + Cl_2 + H_2O \leftrightarrow SO_3 + 2\ HCl$	Chlorine-Griffin-Reaction
$SO_2 + ½\ O_2 \leftrightarrow SO_3$	SO_2/SO_3-Konversion
$Hg + Cl_2 \leftrightarrow HgCl_2$	direct Hg-Chlorination

Chlorine less effective in Hg-oxidation

because $Cl_2/Cl_{total} << 1$

(e.g. < 4 % in HWC and < 1 % in coal combustion)

SO_2 is consuming Cl_2 during boiler passage

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Bromine Enhanced Hg-Oxidation

Relevant global reactions

$4\ HBr + O_2 \leftrightarrow 2\ H_2O + 2\ Br_2$	Bromine-Deacon-Reaction
$SO_2 + Br_2 + H_2O \leftrightarrow SO_3 + 2\ HBr$	Bromine-Griffin-Reaction
$SO_2 + Br_2 + 2\ H_2O \leftrightarrow H_2SO_4 + 2\ HBr$	Bromine-Bunsen-Reaction
$SO_2 + ½\ O_2 \leftrightarrow SO_3$	SO_2/SO_3-Konversion
$Hg + Br_2 \leftrightarrow HgBr_2$	direct Hg-Bromination

Bromine highly effective in Hg-oxidation

because $Br_2/Br_{total} \rightarrow 1$

SO_2 is not consuming Br_2 during boiler passage

(at temperatures > 100 °C)

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Poster-Presentation Vosteen at Air Quality IV Conference, Arlington, September 2003

Martin-Luther-University Halle-Wittenberg

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Bayer

Mercury-Related Chemistry in Waste Incineration and Thermal Process Flue Gases

Bernhard W. Vosteen, Vosteen Consulting GmbH, Cologne (Germany)
Richard Ullrich, WastePro Engineering Inc., Kennett Square, PA

Vosteen's 2003 comment on mercury bromination

Bromine 25 times more effective than chlorine for Hg^{met}-oxidation in waste incineration as well as in coal combustion

Following this presentation at AQ IV some bromine related activities came up in the States as well in industry as in science

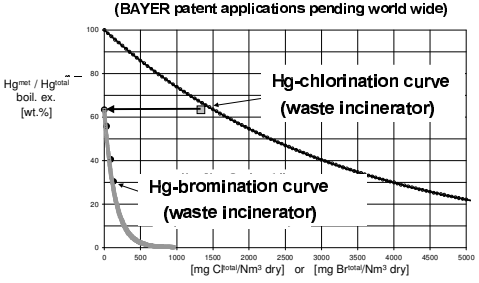
Bromine Enhanced Hg-Oxidation

Main global reactions	(hypothesis Vosteen)	Thermodynamics in boiler temperature range
$4\ HBr + O_2 \leftrightarrow 2\ H_2O + 2\ Br_2$	Bromine-Deacon-Reaction	$\Delta_R G < 0$
$SO_2 + Br_2 + H_2O \leftrightarrow SO_3 + 2\ HBr$	Bromine-Griffin-Reaction	$\Delta_R G >> 0$
$SO_2 + ½\ O_2 \leftrightarrow SO_3$	SO_2/SO_3-Konversion	$\Delta_R G < 0$
$Hg + Br_2 \leftrightarrow HgBr_2$	direct Hg-Bromination*)	$\Delta_R G < 0$
$SO_2 + Br_2 \leftrightarrow SO_2Br_2$	Bromine-Sulfurylisation	$\Delta_R G << 0$
$Hg + SO_2Br_2 \leftrightarrow HgBr_2 + SO_2$	Hg-Bromination by SO_2Br_2	$\Delta_R G < 0$

*) $Hg + 2\ HBr + ½\ O_2 \leftrightarrow HgBr_2 + H_2O$ *indirect Hg-Bromination in boiler not relevant, but in SCR (V_2O_5 as oxigen donator)*

Bromine > 25 times more effective for Hg^{met} oxidation than chlorine in waste incineration as well as in coal combustion

(BAYER patent applications pending world wide)



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Internal US EPRI Report, March 2006

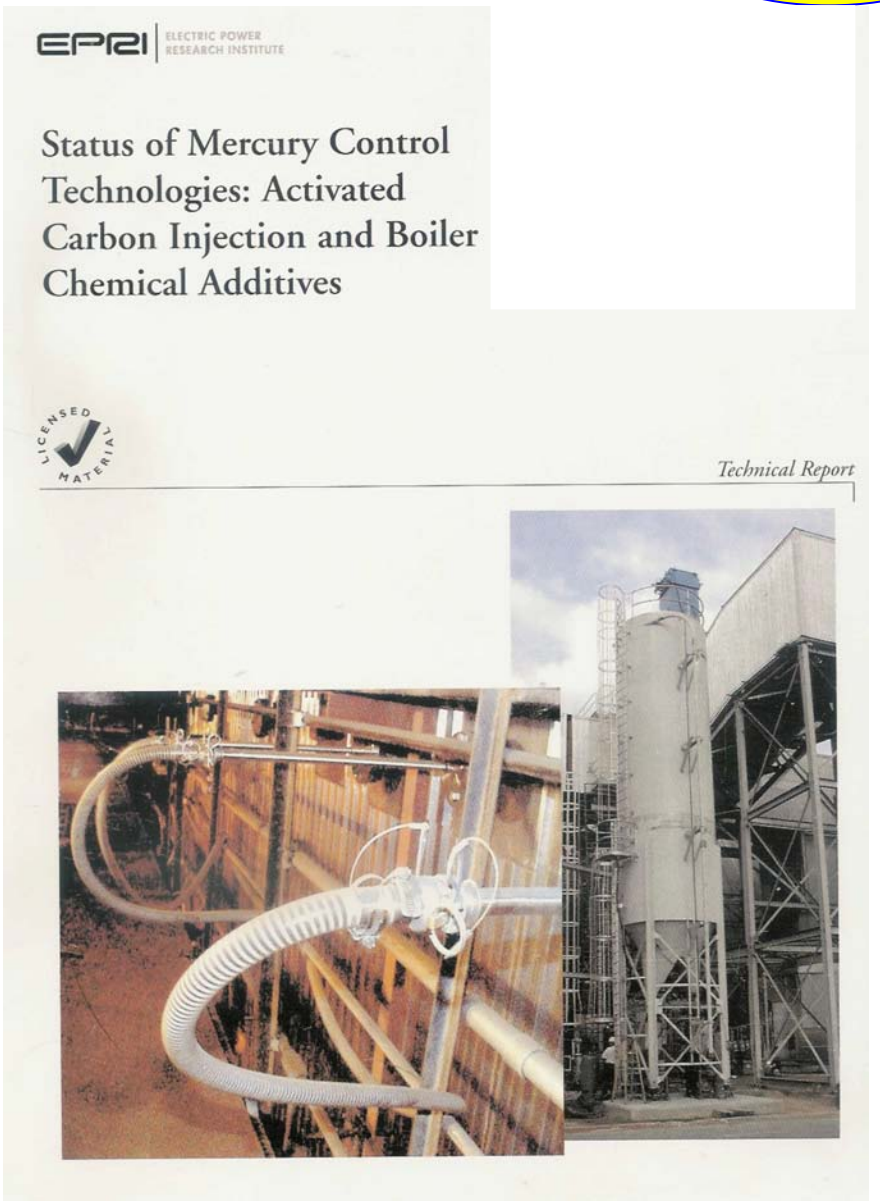
Chapter 3: „Boiler Chemical Additives“

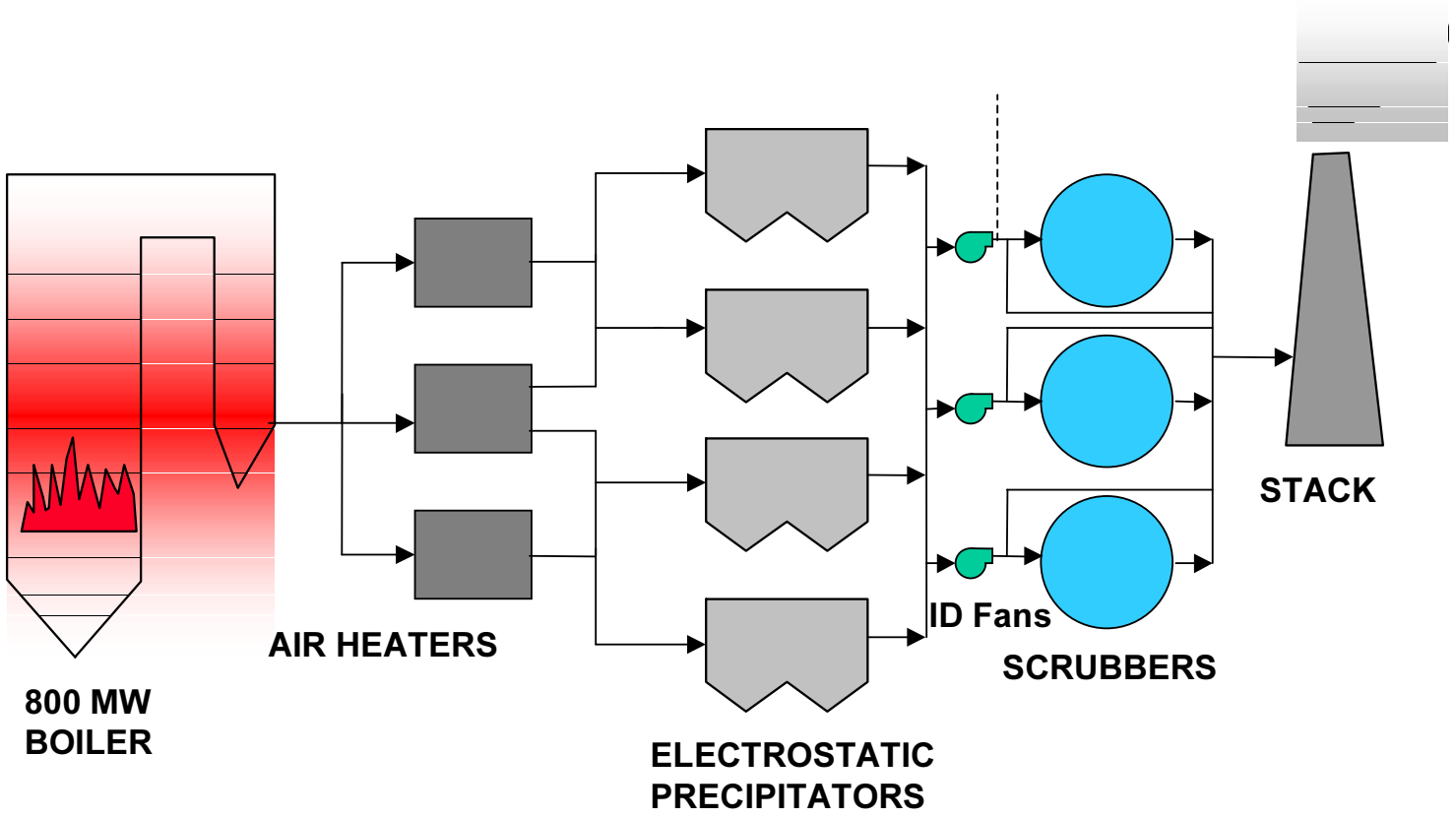
Chemical Addition Tests Performed at Host Sites

Unit	Test Period	Reagents Tested	Addition Method
Laskin 2	May 2002*	NaCl, $CaCl_2$, Fe/NaCl	Solid addition to coal feed
	Sept. 2003*	$MgCl_2$, HCl	Liquid addition to boiler
	Aug. 2005*	$CaCl_2$, $CaBr_2$	Solid addition to coal feed
Meramec 2	Sept. 2004**	KNX, SEA2	Liquid addition to coal feed
Baldwin 3	Aug. 2005*	$CaCl_2$, $CaBr_2$	Liquid addition to boiler
Limestone 1	Sept.–Oct. 2004*	$CaCl_2$, $CaBr_2$	Liquid addition to boiler
Monticello 3	Oct.–Dec. 2005**	$CaCl_2$, $CaBr_2$	Liquid addition to coal feed
Milton R. Young 2	April 2005**	$CaCl_2$, $MgCl_2$, SEA2	Liquid addition to coal feed
Stanton 10	April 2002*	NaCl, $MgCl_2$, $FeCl_2$	Liquid addition to boiler

* - EPRI-conducted tests

** - Tests conducted as part of DOE-NETL Cooperative Agreement Programs

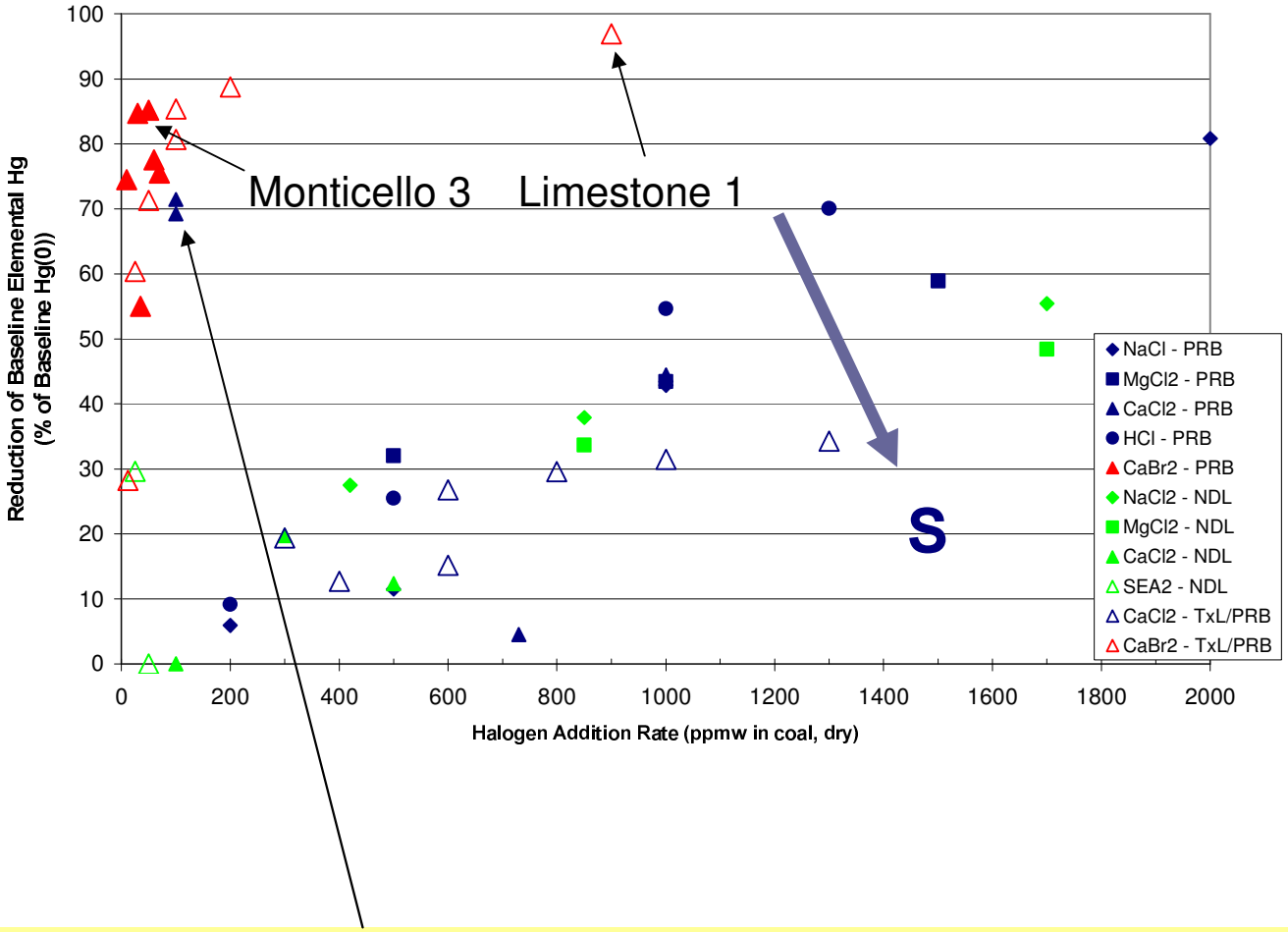




TXU Energy's Monticello Steam Electric Station Unit 3 (793 MWe)

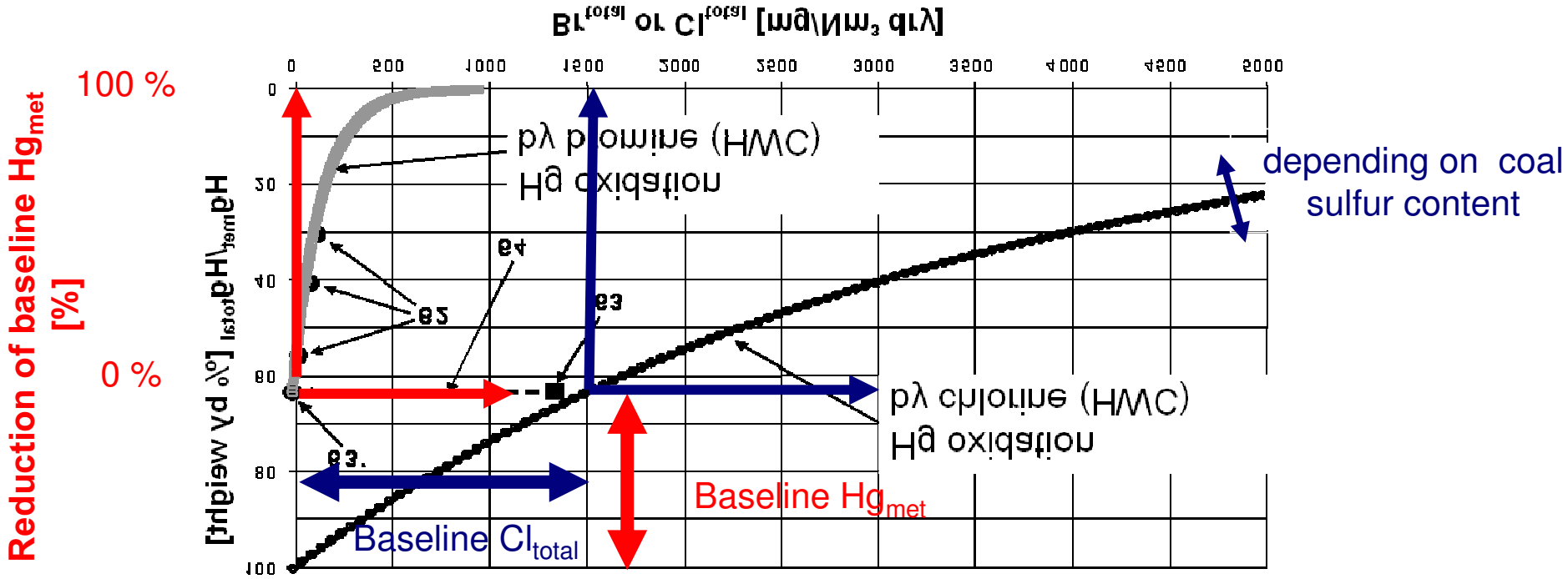
Reduction of Baseline Elemental Mercury

Overview over all sites tested by EPRI in 2002 ... 2005 (chlorine) and repectively 2004 ... 2005 (bromine)



"Halogen containing SEA2 (proprietary), composition not revealed"

bromination **chlorination**



Halogen addition [mg/Nm³ dry]

Comparing Waste combustion with EPRI test runs at PC-fired power stations in 2001 … 2005 (chlorination) and 2004 … 2005 (bromination)

Lower mercury concentration in coal combustion (factor 85/15 = factor 6) and 6.5 Nm³ dry/kg PRB ->

The comparison shows that the results attained at the HWC are not only qualitatively the same, but quantitatively too!

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University R&D:

VOSTEEN Consulting GmbH

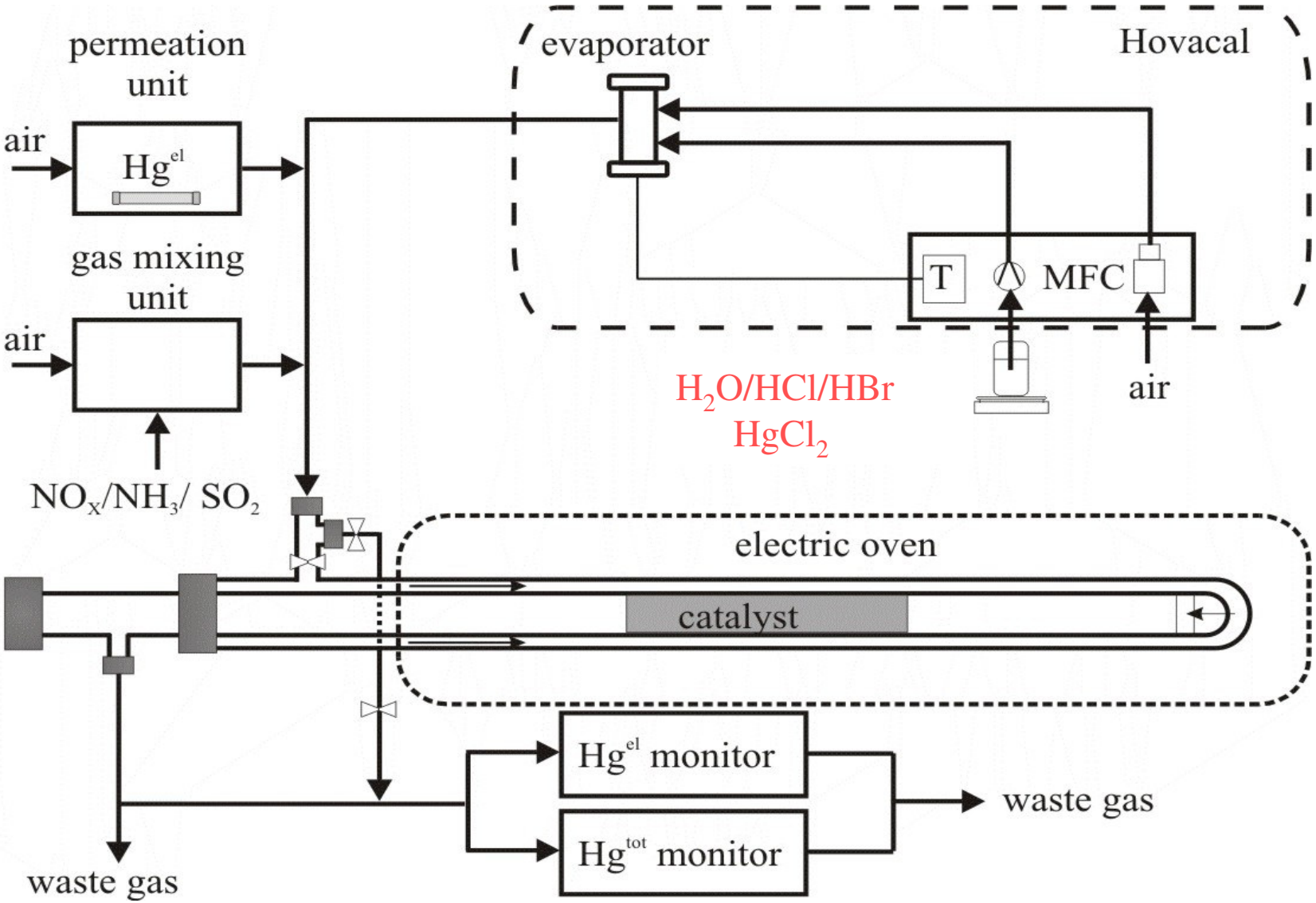
Thermal Engineering and Environmental Protection

Martin-Luther-Universität Halle-Wittenberg

Martin-Luther-University Halle-Wittenberg
Institute for Environmental Engineering
Heinz Köser, Bernhard Vosteen, Rico and Ewa Kanefke, Sandra Straube, Martin Ziegler et al.

TUClausthal

Technical University Clausthal
Institute for Energy Process and Fuel Technology
Roman Weber, Bernhard Vosteen, Michael Nolte et al.


permeation unit
air
Hg^el
gas mixing unit
air
NOx/NH3/ SO2
evaporator
Hovacal
T
MFC
air
H2O/HCl/HBr
HgCl2
electric oven
catalyst
Hg^el monitor
Hg^tot monitor
waste gas
waste gas

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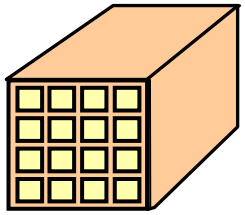
Presented at EUEC 2006:

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

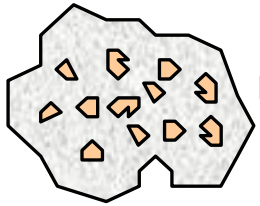
0 - 0,53 - 2,5 - 4,5 Ma.-% V2O5

0 - 2000 µg Hg/Nm³



ca. 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

post graduate research work by Dipl.-Ing. Sandra Straube

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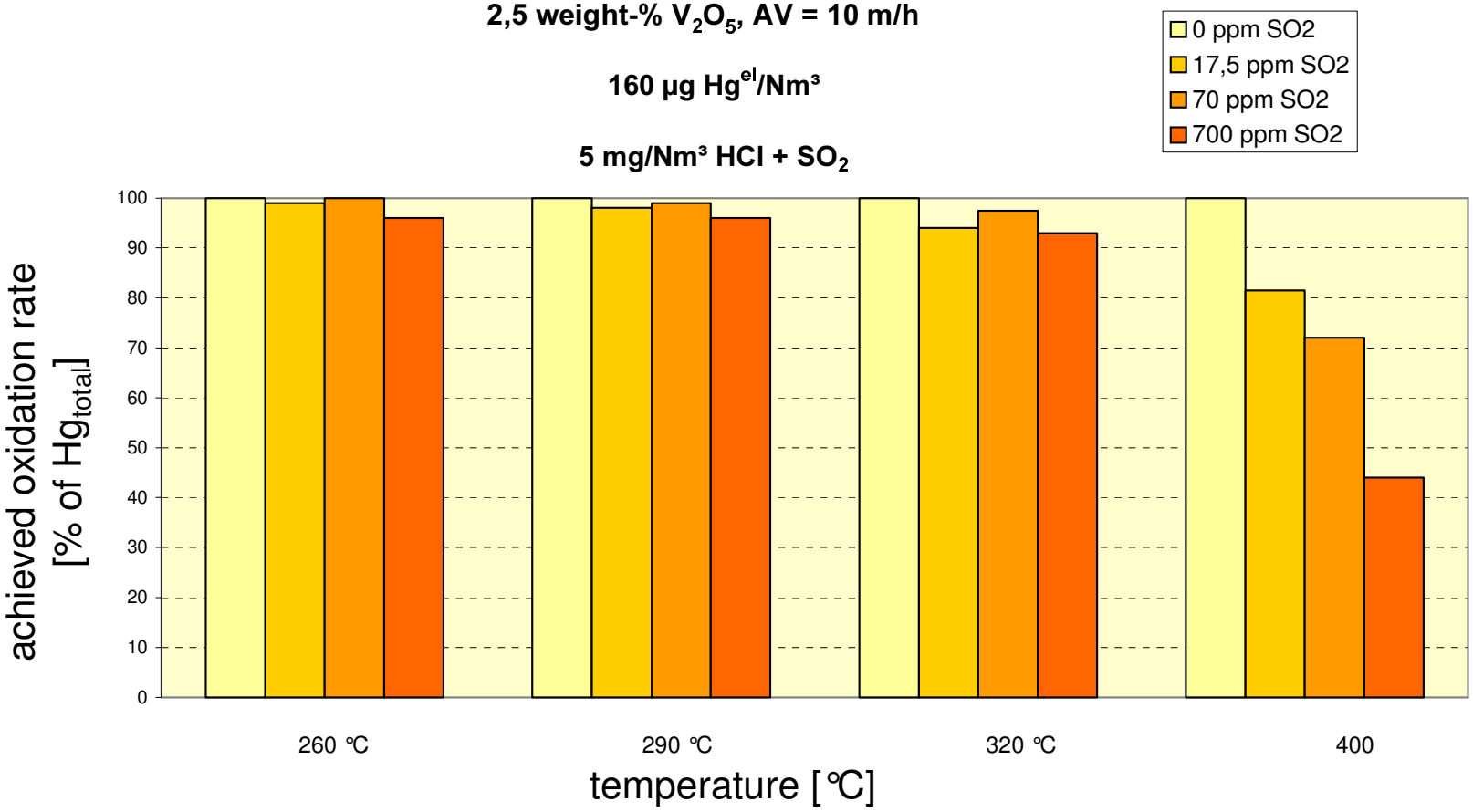
Honeycomb catalyst

4 x 4 canals, 12.5 cm long

2,5 weight-% V_2O_5, AV = 10 m/h

160 µg Hg^{el}/Nm³

5 mg/Nm³ HCl + SO_2



Laboratory tests with humid air, 160 µg Hg^{el}/Nm³ dry and ***5 mg HCl/Nm³*** *added*

(no NH_3 and no NO_x)

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

Influence of Cl_2 and SO_2 on mercury chlorination at SCR catalyst (not denox-active)

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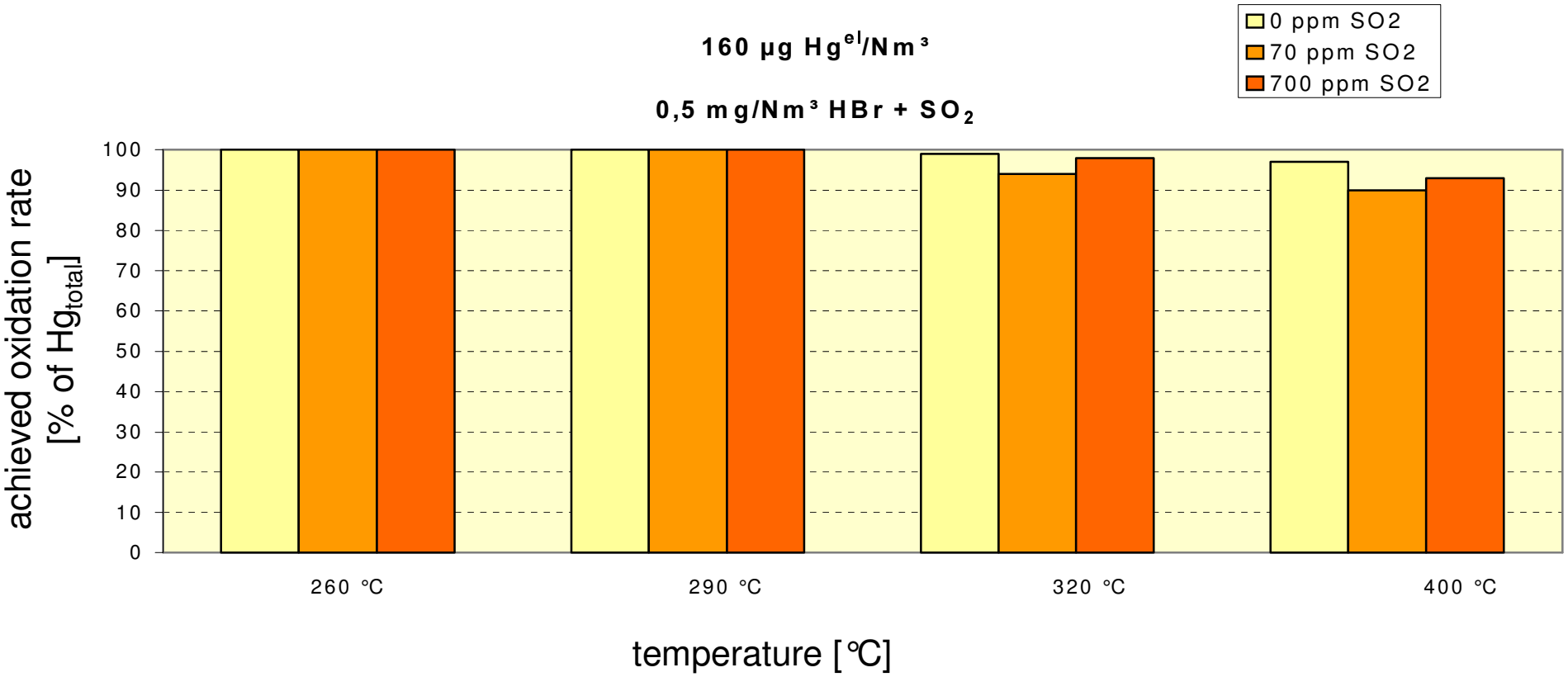
Honeycomb catalyst

4 x 4 canals, 12.5 cm long

2,5 weight-% V_2O_5, AV = 10 m/h

160 µg Hg^{el}/Nm^3

0,5 mg/Nm^3 HBr + SO_2



Laboratory tests with humid air, 160 µg Hg^{el}/Nm^3 dry and ***only 0.5 mg HBr/Nm^3*** *added*

(no NH_3 and no NO_x)

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

Influence of temperature and SO_2 on Hg-bromination at the not denox-active SCR catalyst

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In Plant research in 2001

high Hg_{total} in the flue gas (9600 µg Hg/Nm³ dry)

Mass ratio for complete mercury removal

Br/Hg = 500 ("without SCR")

Laboratory research in 2005

low Hg_{total} in the flue gas (160 µg Hg/Nm³ dry)

Mass ratio for complete mercury removal predicted*)

Br/Hg ≥ ca. 50 ("with SCR")

*) Vosteen, B., Straube, S., Koeser, H.: "Mercury Sorption and Mercury Oxidation by Chlorine and Bromine at SCR DeNOx Catalyst", Parts A and B, EUEC 2006

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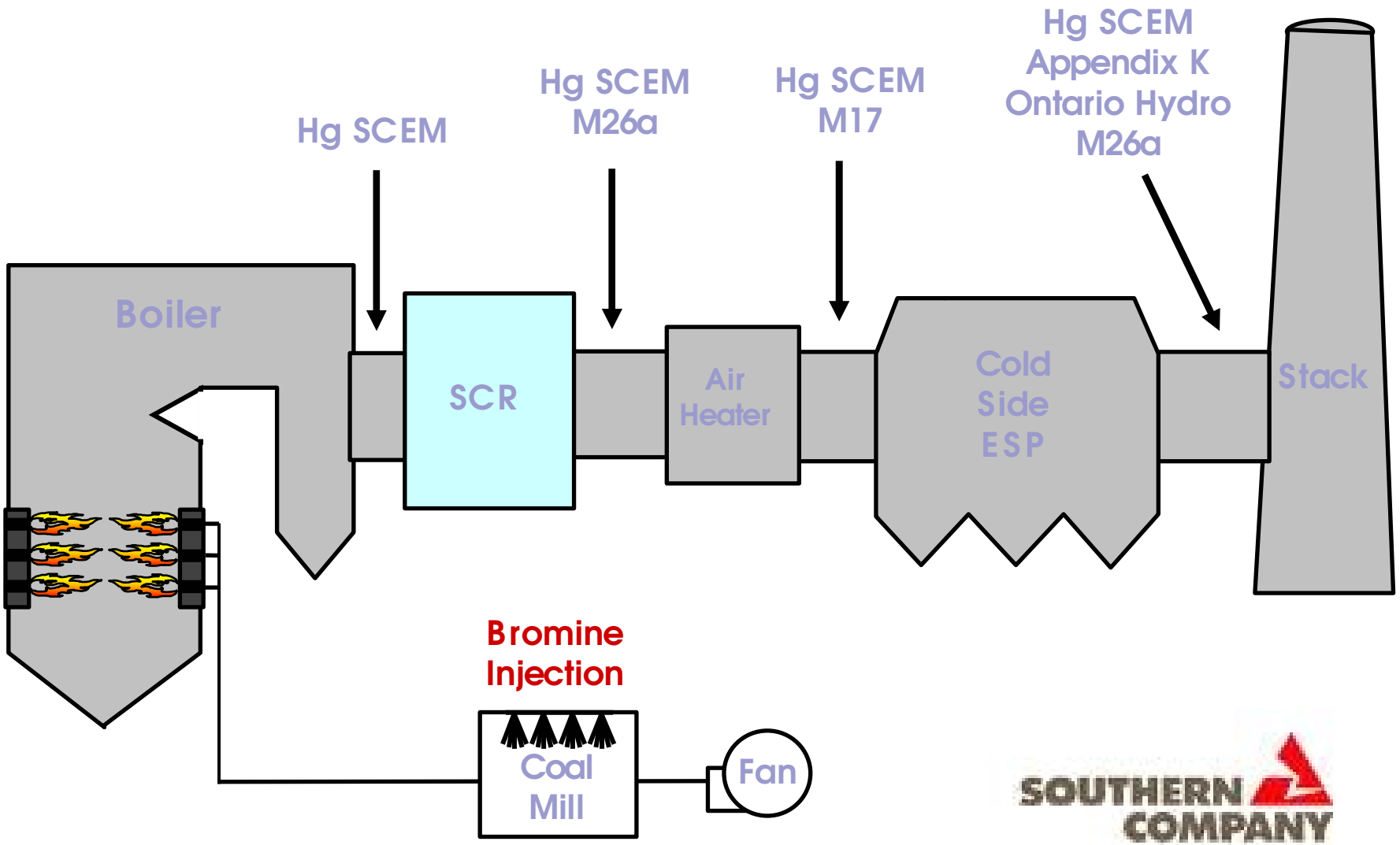
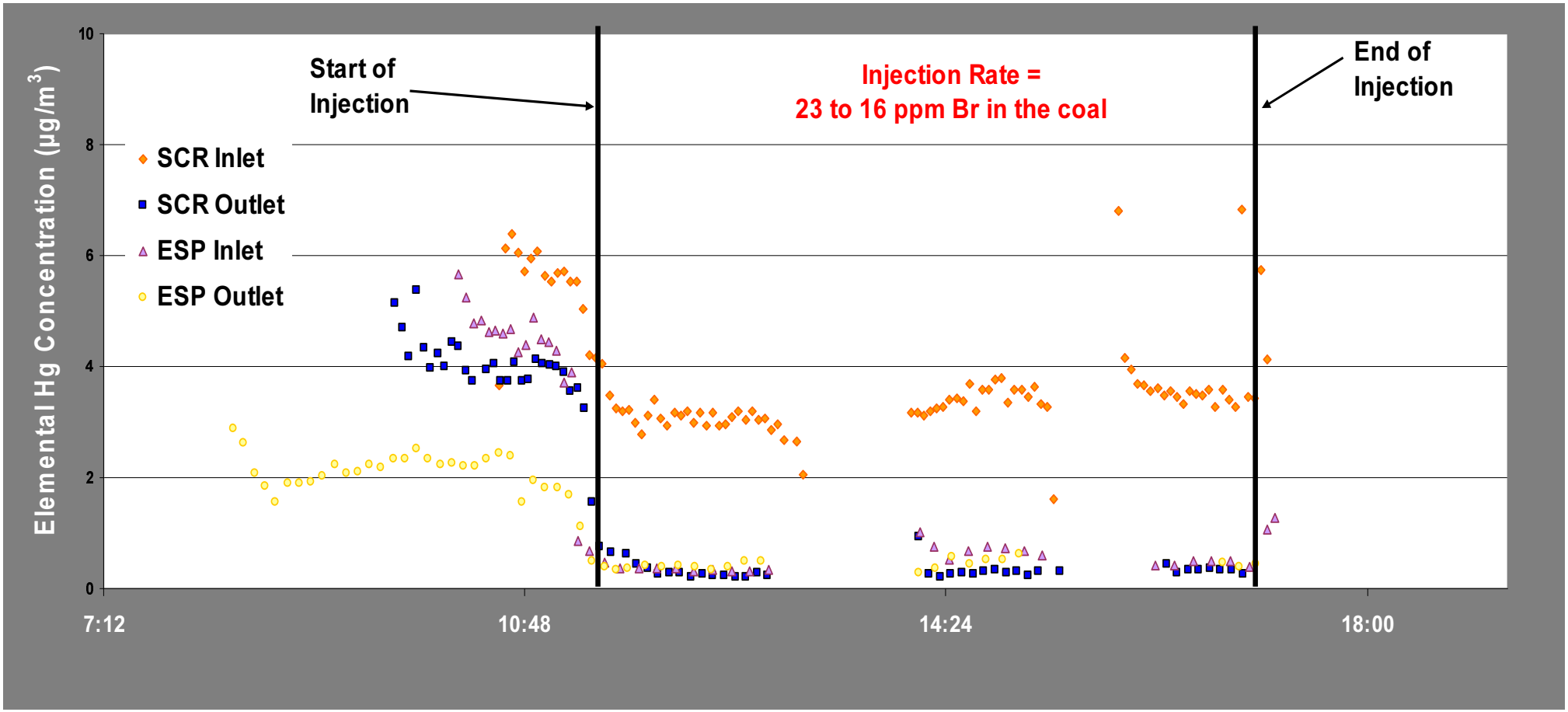
Miller Measurement Locations



SOUTHERN COMPANY
Energy to Serve Your World℠

Miller Testing Results
Low Bromine Injection Test



0.5 – 1.0 ppmv Br Concentration

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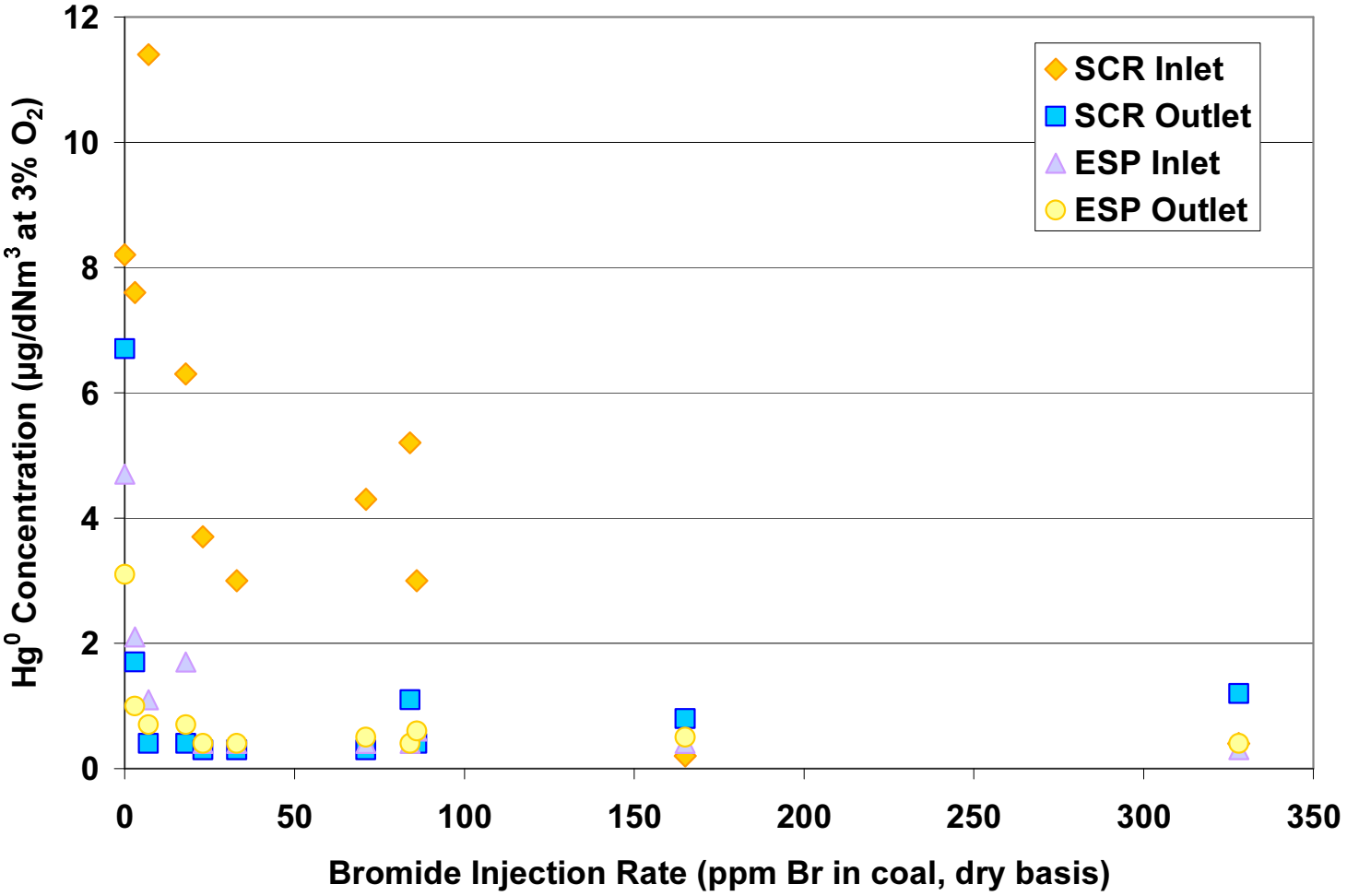
Miller Average Elemental Mercury Concentrations Measured During Each Bromide Injection Test



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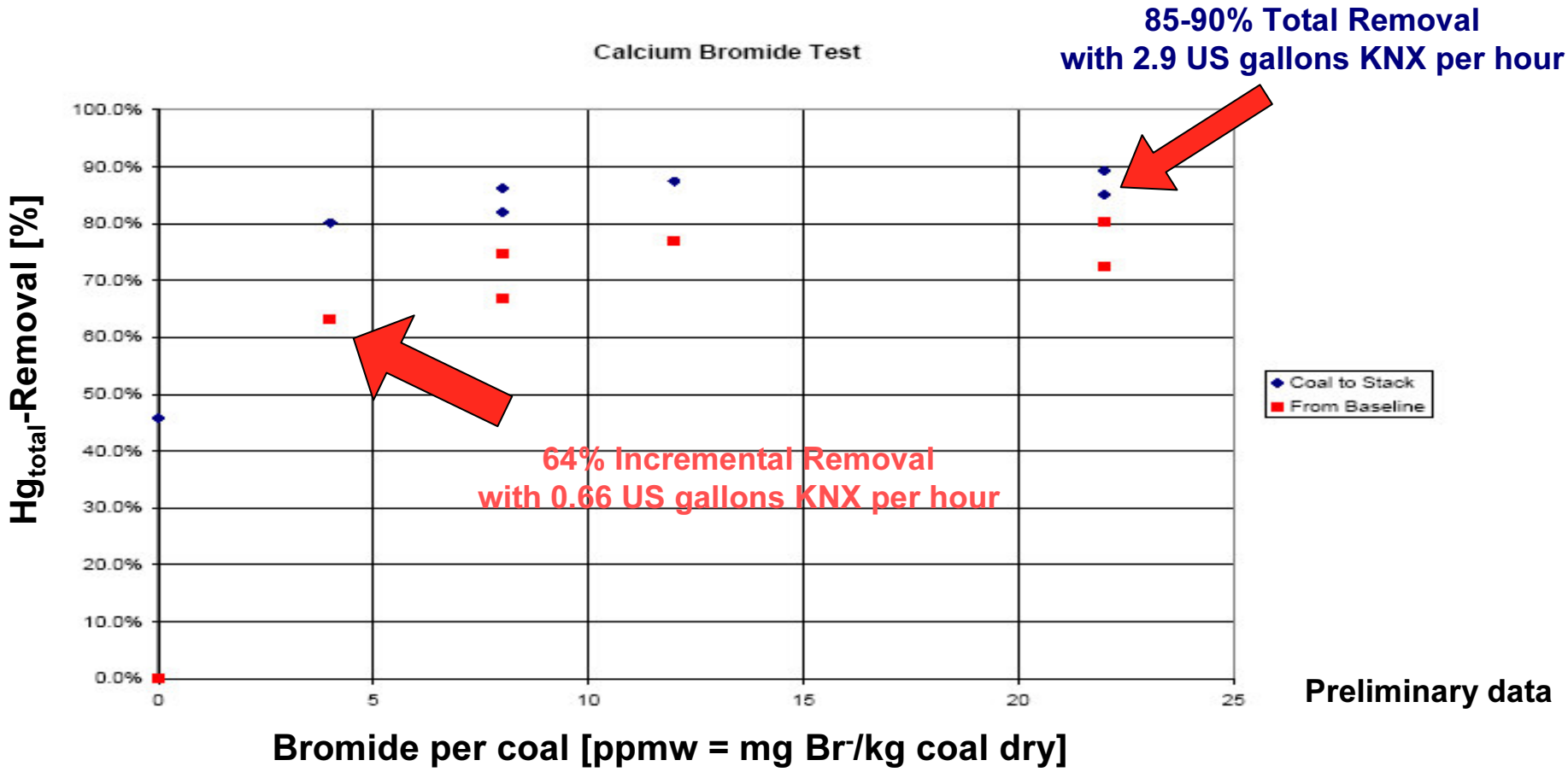
600 MWe, PRB coal, SCR/ESP/WFGD

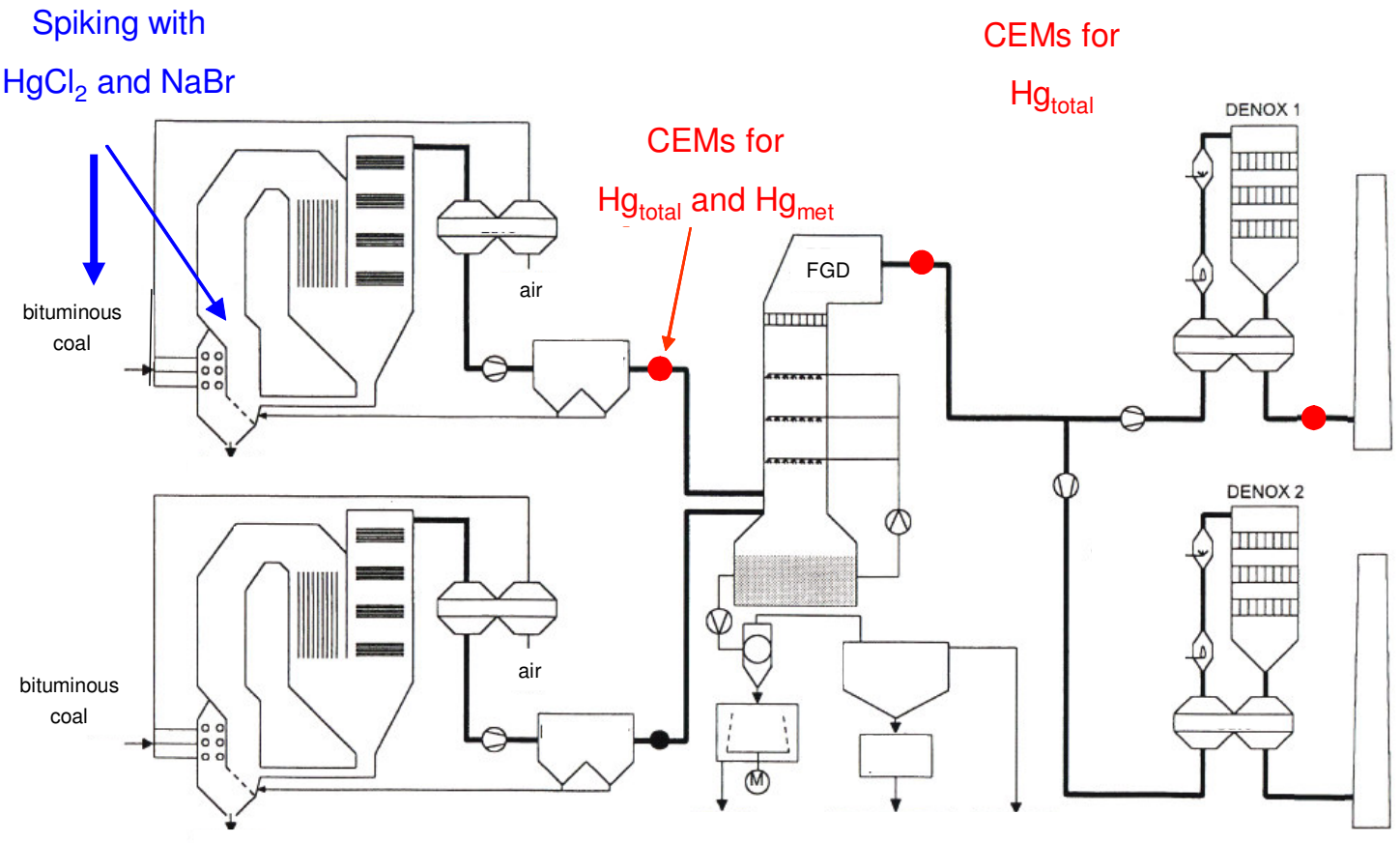
315 t PRB coal/ h, 0.11 mg Hg/kg coal



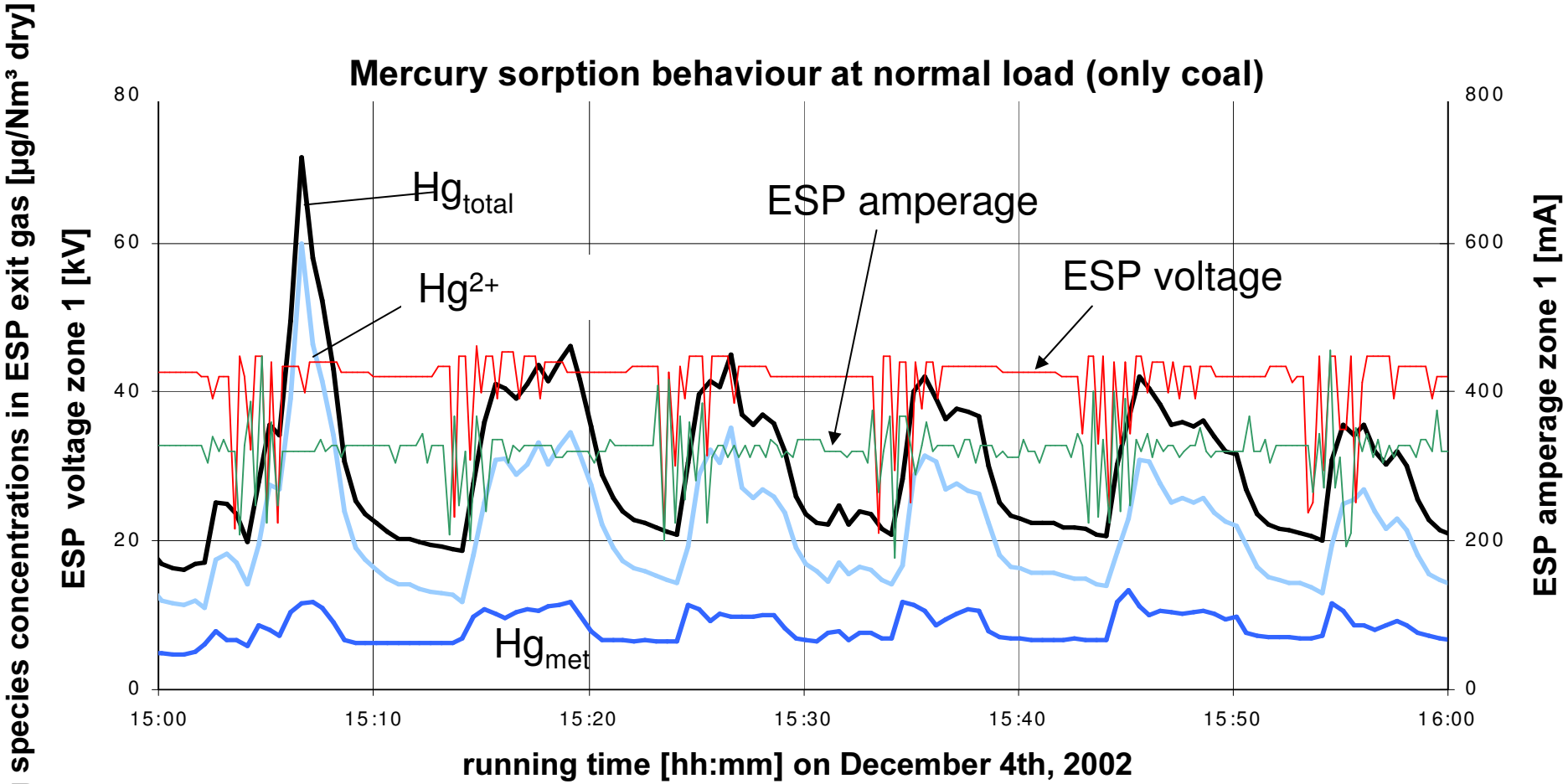
M. J. Rini at DOE NETL Conference, Pittsburgh, December 2007

ALSTOM

- **First Industrial Demonstration in 2002 (2 x 5 days testing) diploma thesis of Michael Nolte**
  PC-fired Wet Bottom Boiler (100 MW_{therm}; 140,000 Nm^3/h dry) of BAYER AG in Uerdingen (Germany), ESP, limestone based wet FGD, tail end DeNOx-SCR



diploma thesis of Michael Nolte, 2002



Mainly ionic mercury is adsorbed at ESP fly ash,

preferably at the fly ash covering the plate electrodes

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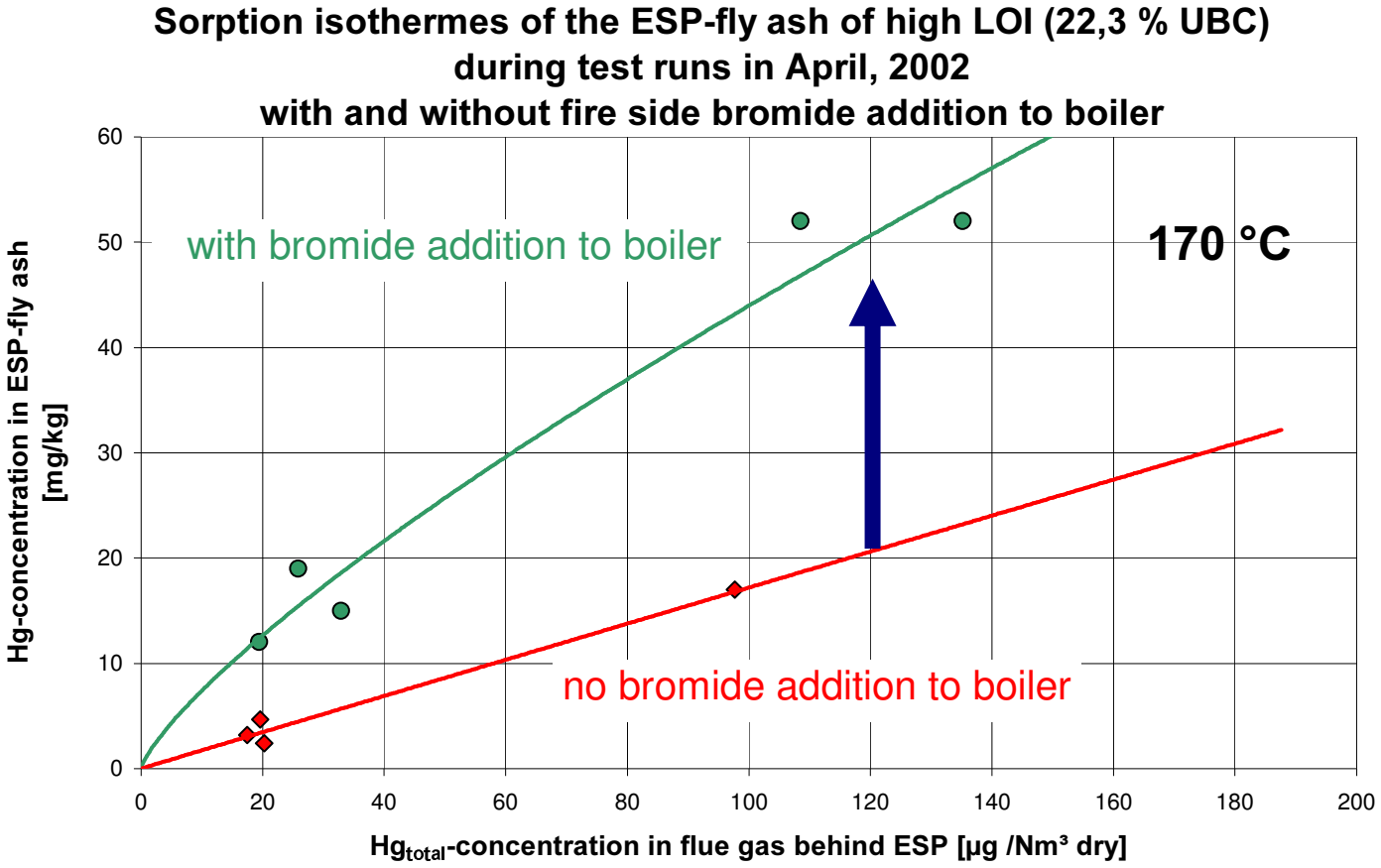
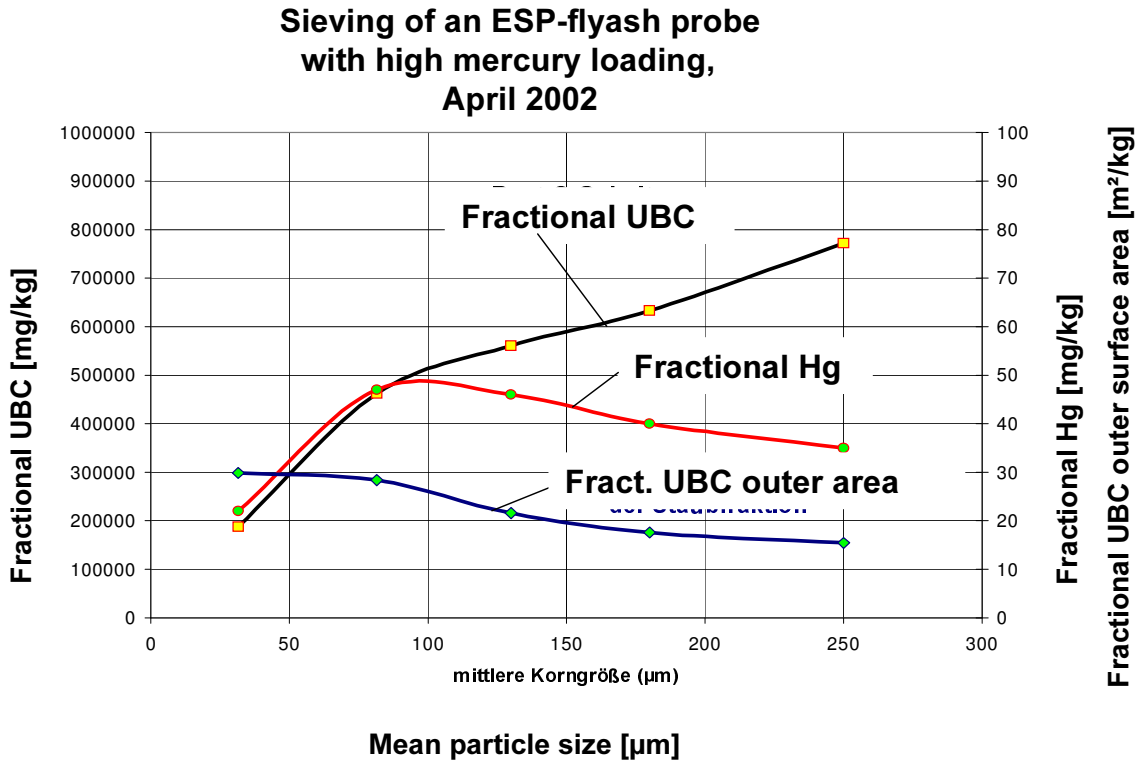
diploma thesis of Michael Nolte, 2002



Fire side bromide addition (internal bromination)
is improving Hg-adsorption at fly ash UBC by the factor 2,5

Particle size distribution of UBC and mercury in the ESP-flyash



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Conclusions

„Complete Mercury Oxidation“ achieved by KNX in Waste Combustion and in Coal Combustion

1. without SCR at a mass ratio Br/Hg > 500
2. with SCR at a mass ratio Br/Hg ≥ 50

Based on enhanced mercury oxidation,

KNX is improving considerably both

absorptive and adsorptive mercury capture too,

as already demonstrated in 2002

Thanks for Your attention

Questions?