PAN|CHEMIE

VOSTEEN Consulting

54th POWER PLANT COLLOQUIUM
at October 18th and19th, 2022
International Congress Center Dresden

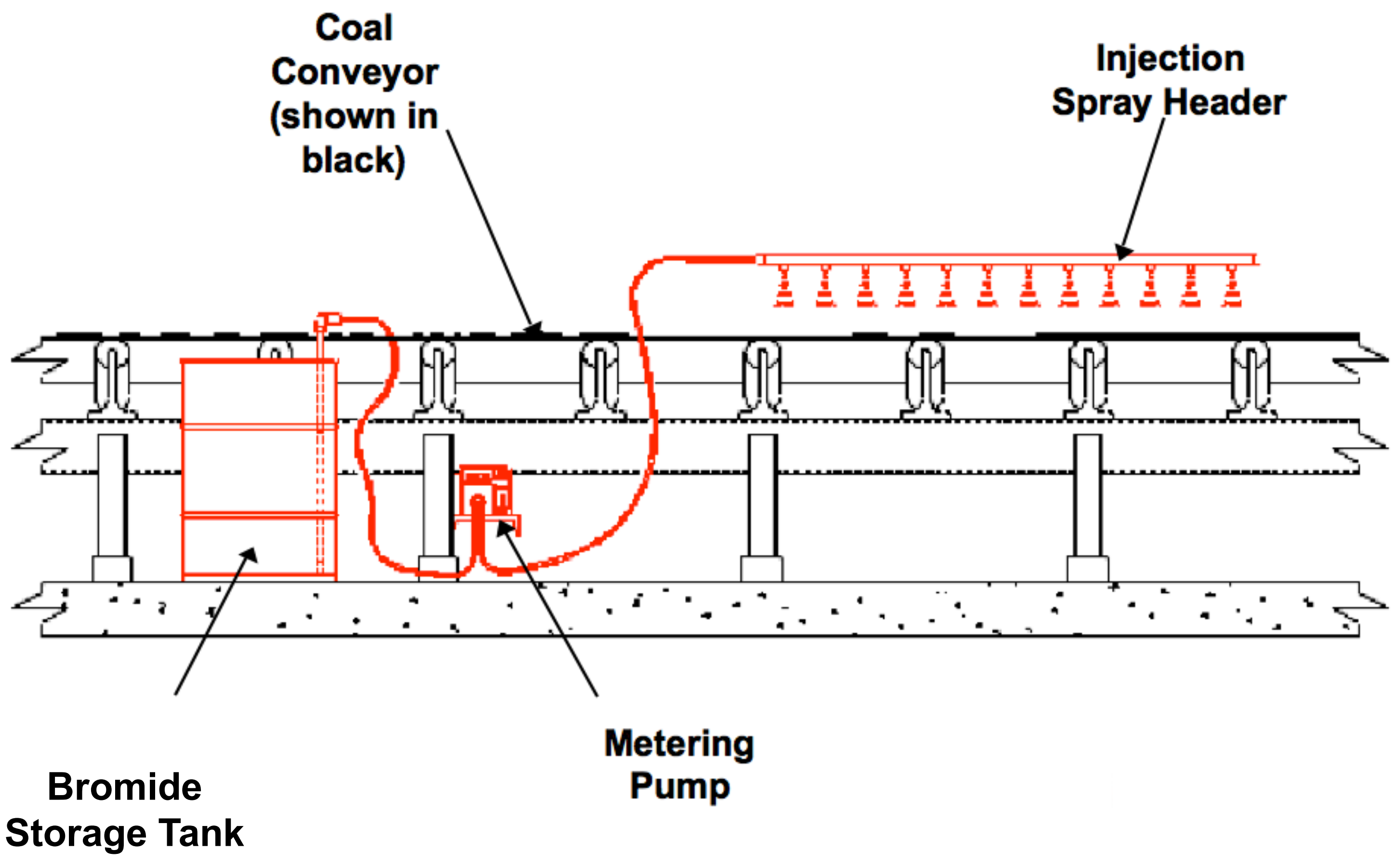
The BEMO-Technology combined with NOx-Reduction up- and downstream of HCl- and SOx- Air Polution Control Systems

***Prof. Dr.-Ing. Bernhard Vosteen**,*
Vosteen Consulting GmbH, Köln

Agenda

1. Introduction – the use of $CaBr_2$ as oxidizer and PRAVO® as stabiilisator
2. Plants with SCR-Systems in various positions
   - Plants with Tail-End-SCR at waste- and coal-combustion sites
   - Plants with high-dust-SCR at at waste- and coal-combustion sites
3. Plants with SNCR and/or Staged Combustion only
4. Conclusions

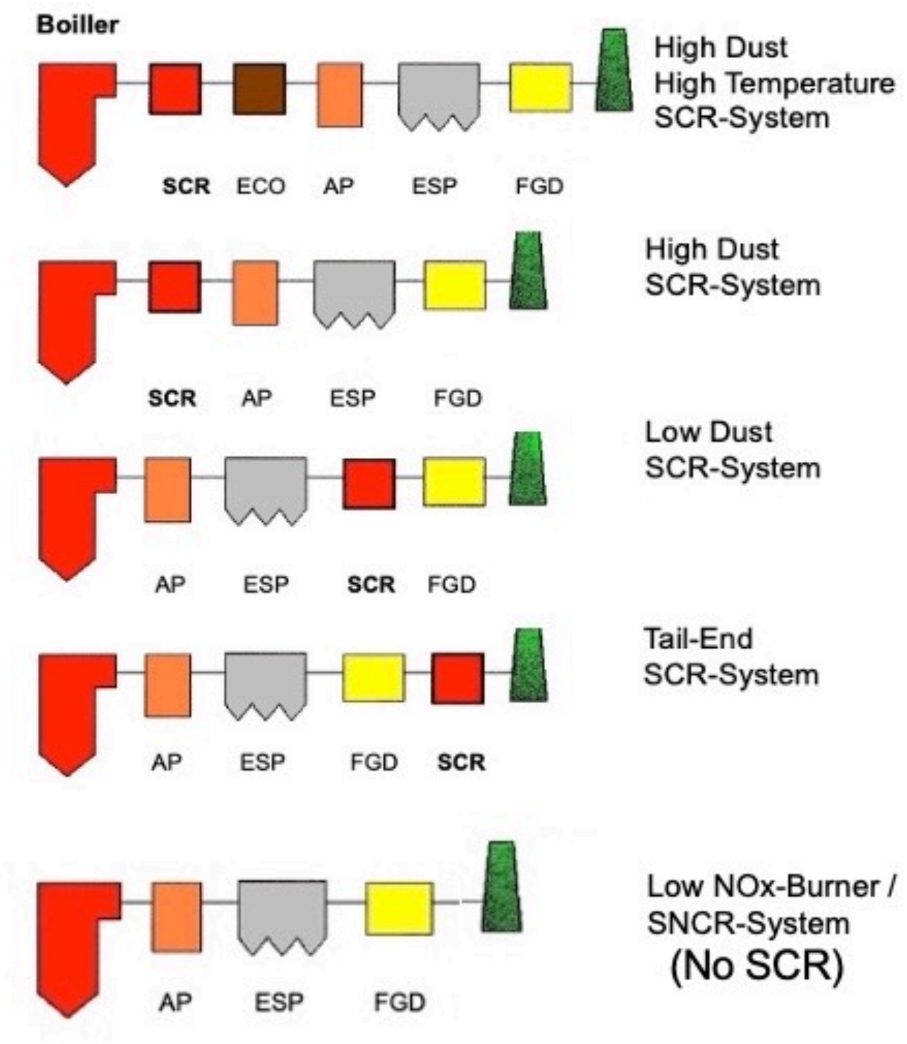
Bromine-based Mercury Oxidation (BEMO) – Bromide addition on coal conveyor belt



Typical US Coal Compositions

Type	Cl content	Hg content
Lignite	Low	High
Sub-bituminous	Low	Low
Bituminous (Western)	Medium	Low
Bituminous (Eastern)	High	Medium
PRB	Low	Medium

BEMO-Technology combined with DeNOx-Technology



Bituminous and Subbituminous Coal

Waste, Subbituminous Coal

Hazardous Waste MSW, Coal

Lignite Sewage Sludge

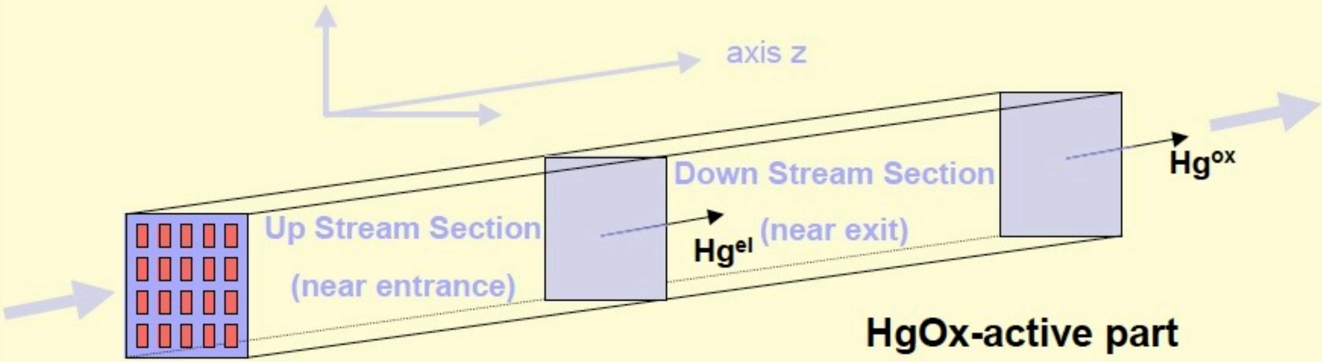
Hg-related R&D at Institute Prof. Dr.-Ing. habil. Heinz Köser

In cooperation with Prof. Bernhard Vosteen

Up and Down Stream Sections of a SCR DeNOx catalyst bed

***Low AV** [Nm³/(m² hr) = m/hr] **or corresponding low SV** [Nm³/(m³ 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., VGBPowerTech (2003)

post-graduate research by Dr.-Ing. Raik Stolle

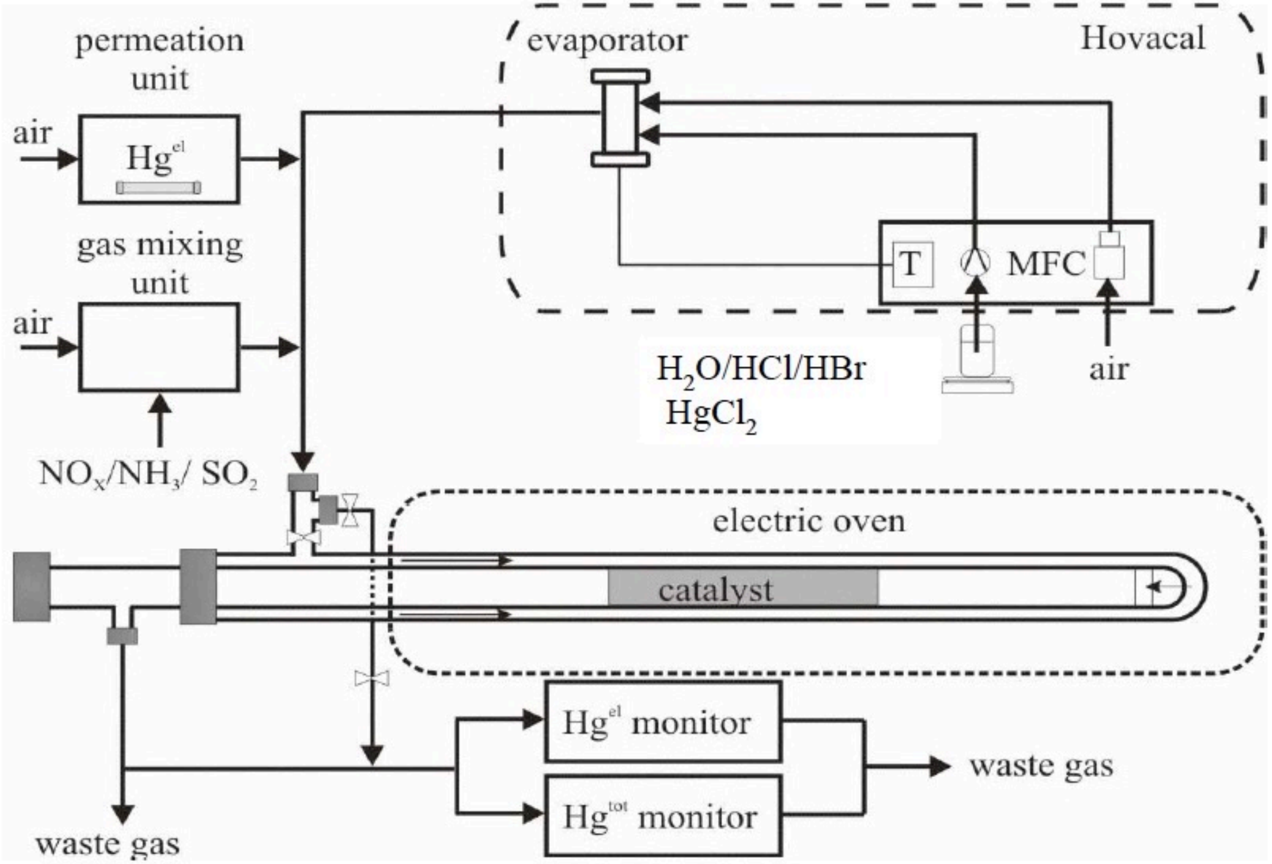
Gas Mixing and Gas Analyzer Station

Prof. Heinz Koeser and Prof. Bernhard Vosteen
at Martin-Luther University Halle-Wittenberg (Germany)

post graduate research by Dipl.-Ing. Sandra Straube

Hg-related R&D at Institute Prof. Dr.-Ing. habil. Heinz Köser

supported by Currenta and Prof. Bernhard Vosteen



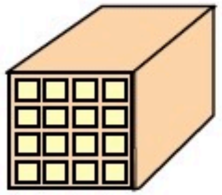
post graduate research by Dipl.-Ing. Sandra Straube

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

commercial SCR-DeNO$_x$-catalysts

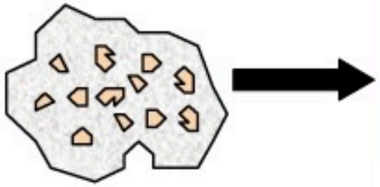
0 - 0,53 - 2,5 - 4,5 Ma.-% V_2O_5

0 - 2000 µg Hg/Nm³



ca. 15 g … 31 g

4 x 4 channels 6,5 … 13 cm long



2 x 0,5 g

Post-graduate reasearch by Dr.-Ing. Sandra Straube

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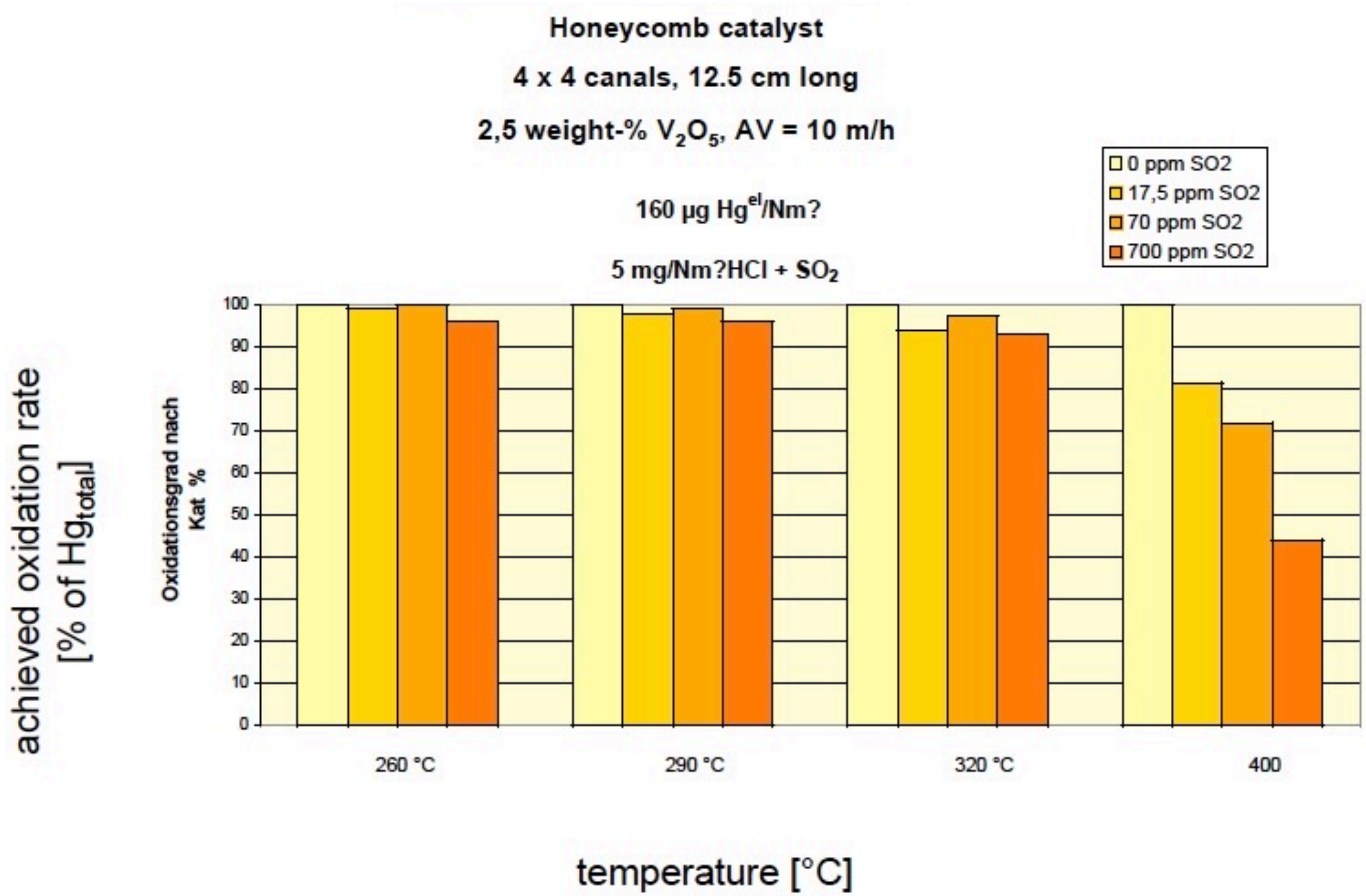


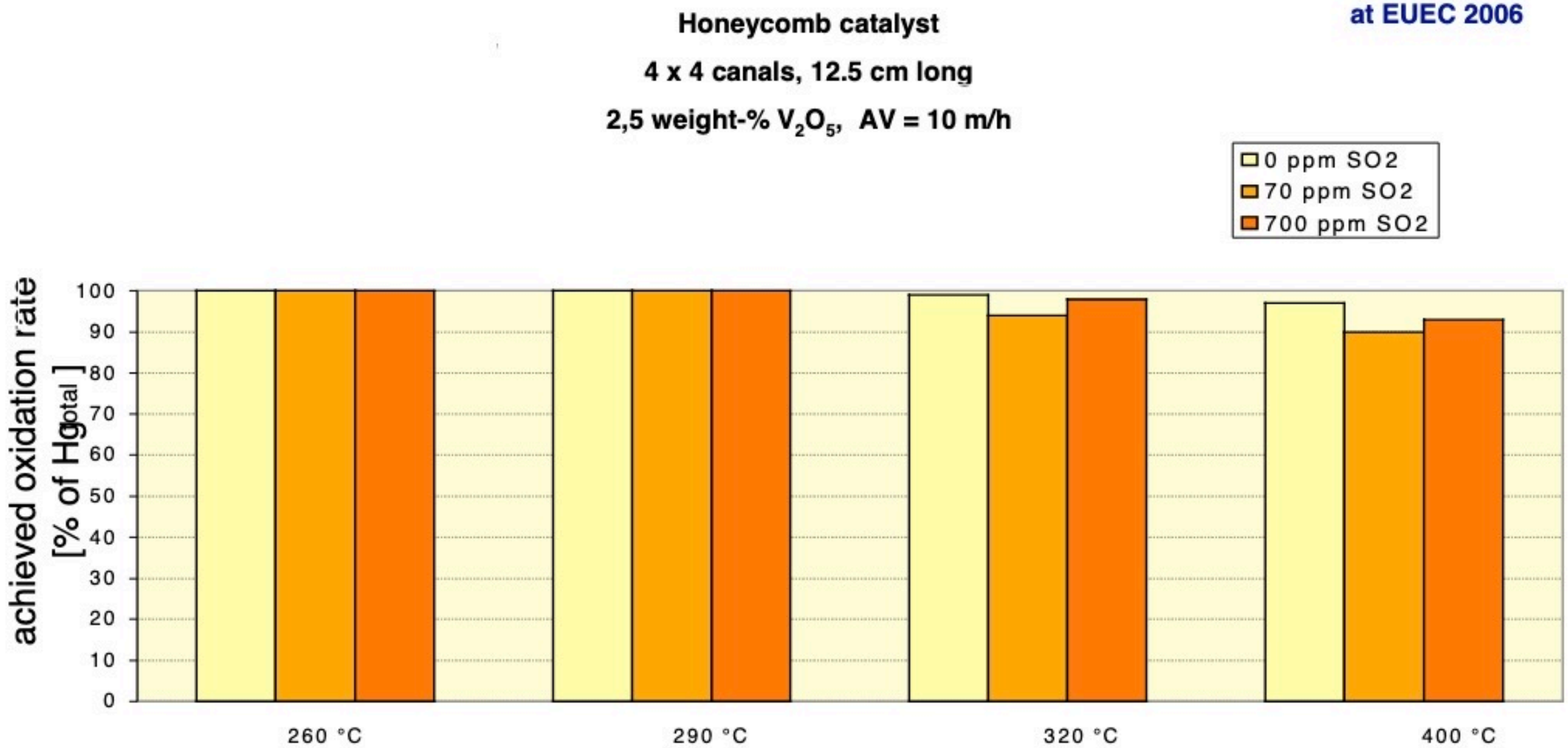
Laboratory tests with humid air, 160 µg Hg^{el}/Nm^3 dry and ***5 mg HCl/Nm^3*** *added*

(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)

presented at EUEC 2006



*Laboratory tests with humid air, 160 µg Hg^{el}/Nm³ dry and **only 0.5 mg HBr/Nm³** added (no NH_3 and no NO_x)*

In contrast to Hg-chlorination, only small influence of temperature and SO_2 on enhanced Hg-bromination at SCR catalyst

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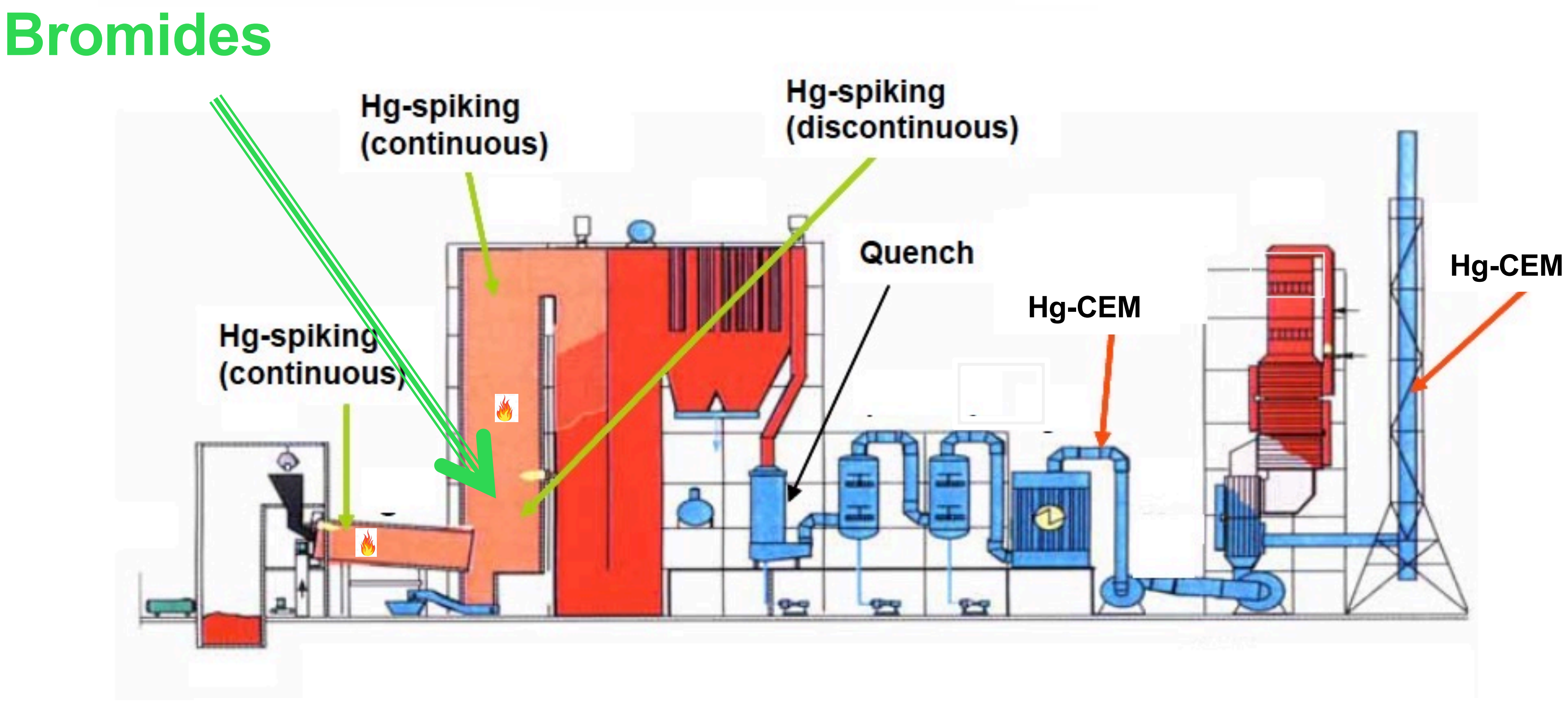
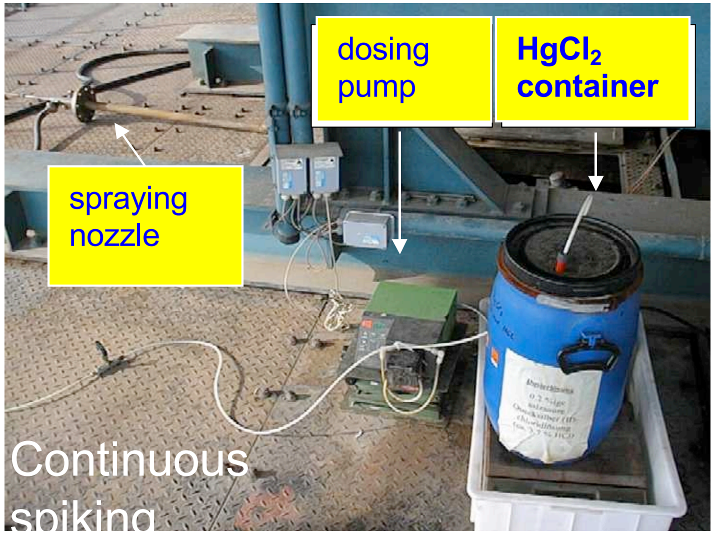
Staged Combustion of Hazardous Waste at Rotary Kiln Incinerators and Nox-Abatement by tail-end-SCR

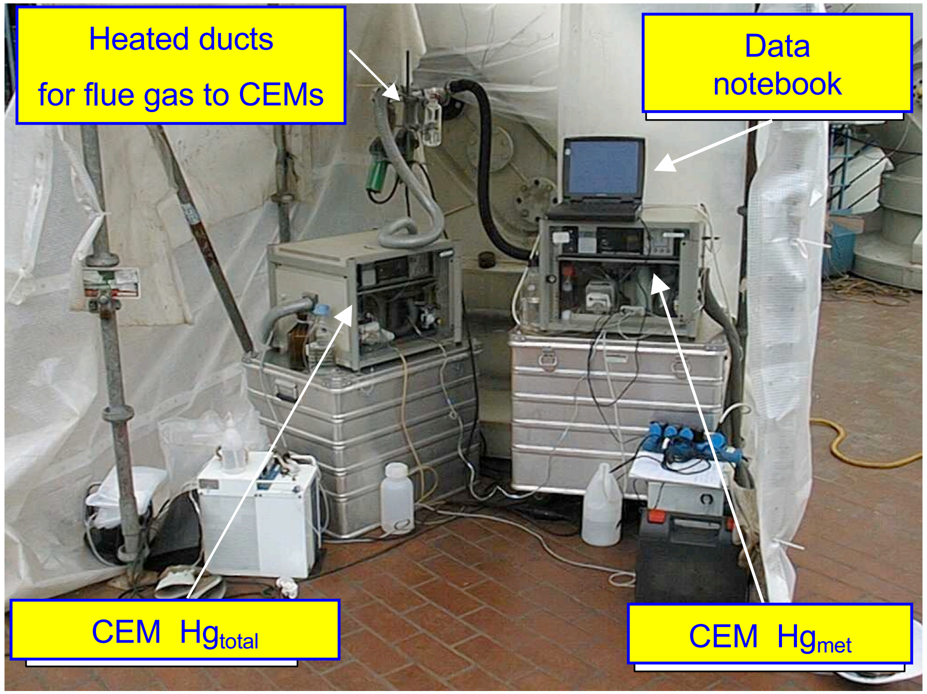
„Bromine-enhanced Mercury Oxidation“at all Bayer WtE-sites (2000) injecting bromide solutions (HBr, NaBr, $CaBr_2$)s



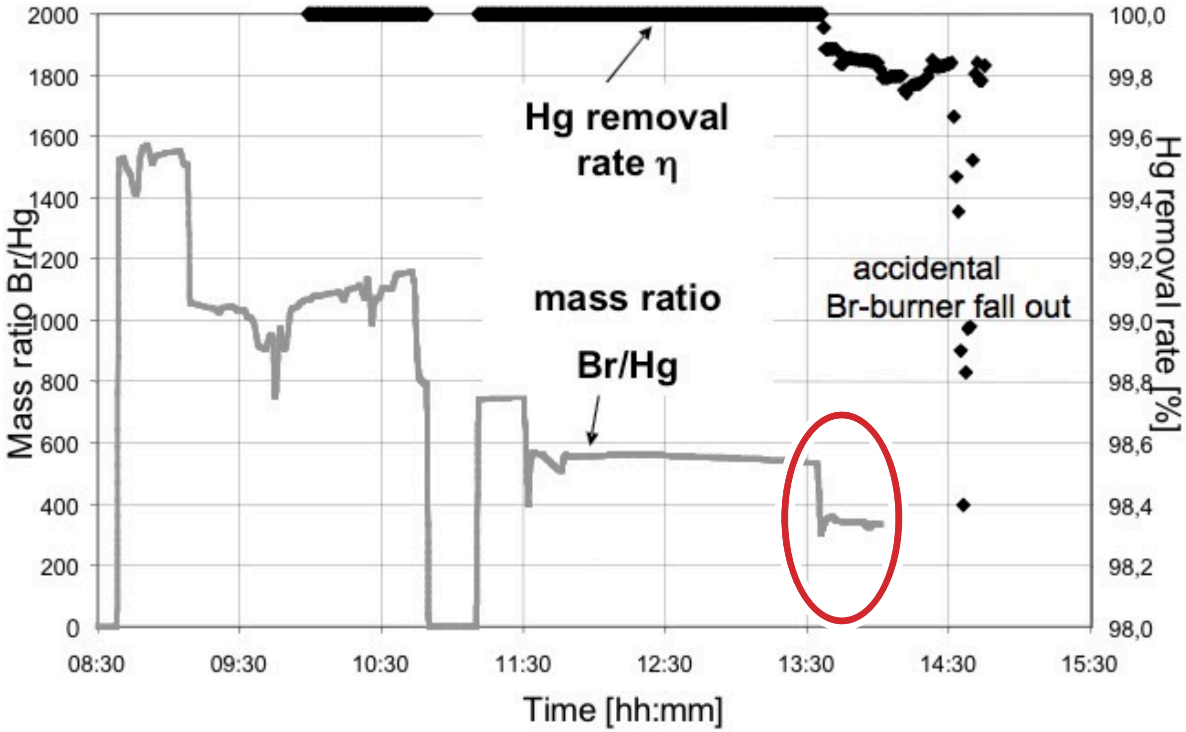
Invention Prof. Vosteen (2000)


dosing pump
$HgCl_2$ container
spraying nozzle
Continuous spiking


Hg_{met} bomb
Discontinuous spiking


Heated ducts for flue gas to CEMs
Data notebook
CEM Hg_{total}
CEM Hg_{met}

Spiking the boiler raw gas with 9600 μg Hg/Nm³ dry)



Mass ratio Br/Hg = 100 … 500 needed
("without high dust SCR")

Retention of Hg° in tail-end SCR

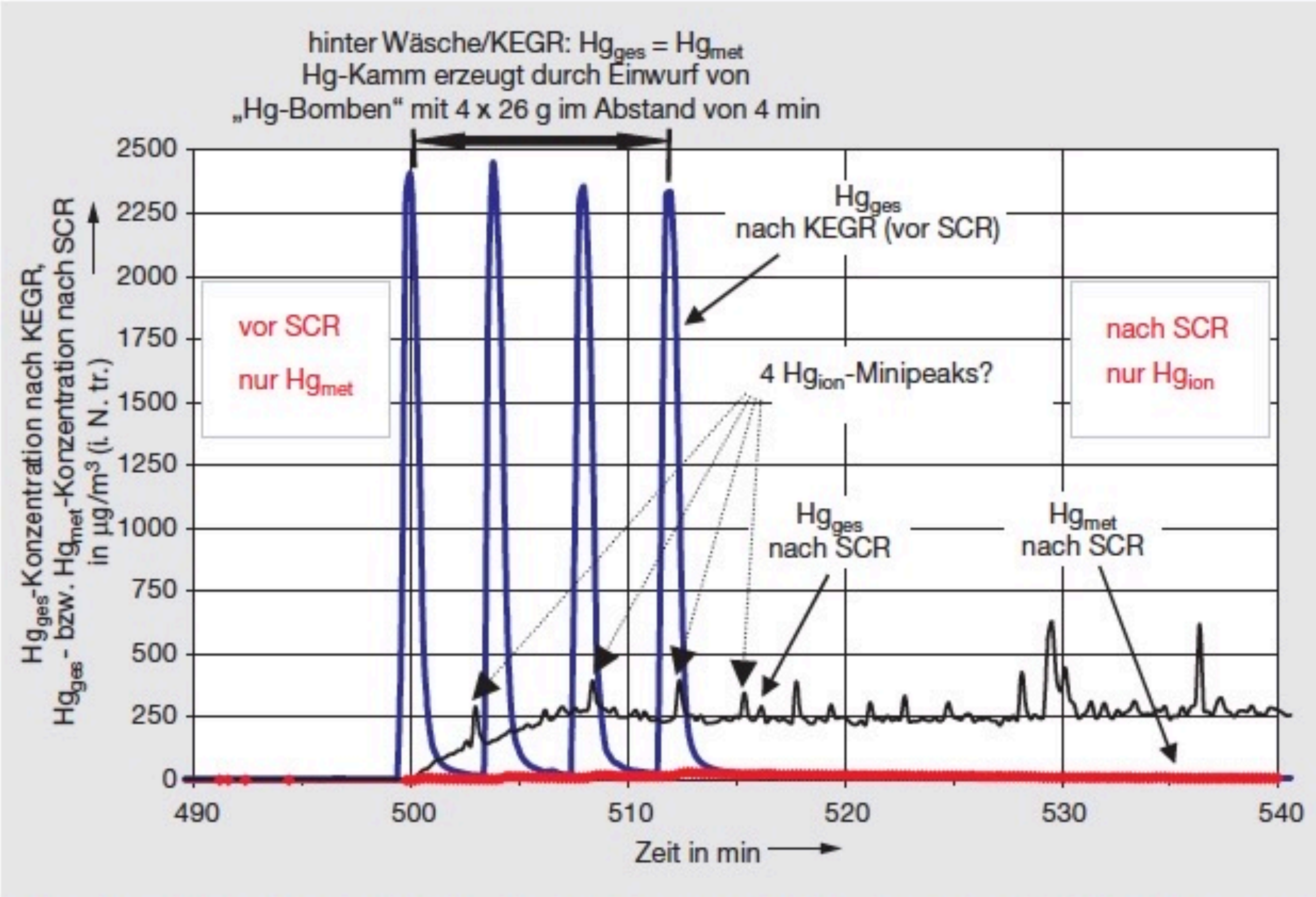


Bild 4. Versuch an Anlage A (Anlage B außer Betrieb) mit einem gezielt erzeugten Hg-Bomben-Kamm zum anschaulichen Nachweis der Hg-Retention in der Tail-end-SCR (Abszisse: laufende Tageszeit t ab 00.00 Uhr am 15. Juni 2000, vormittags).

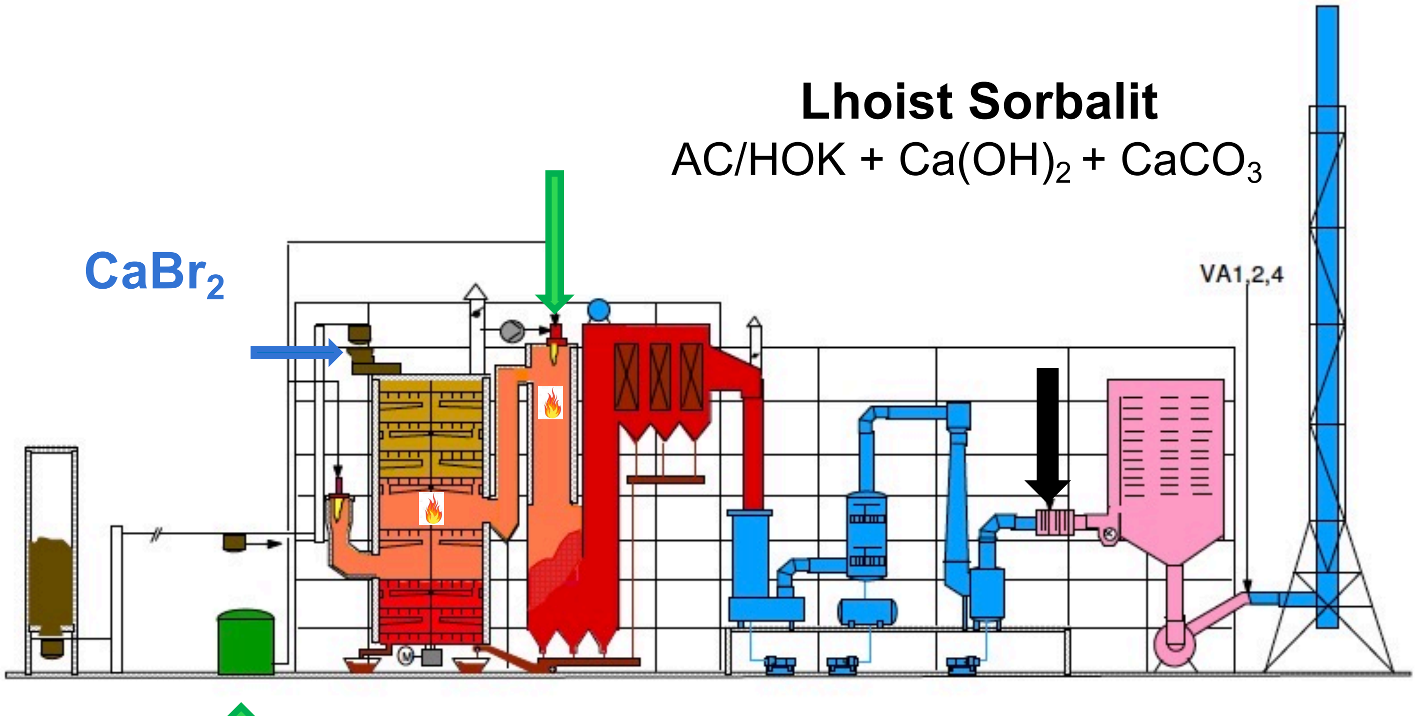
Staged Combustion of Sewage Sludge at Multiple Hearth Furnace and NOx-Abatement by SNCR (1997)

Bromine-based Mercury Oxidation (2000)

Lhoist Sorbalit

AC/HOK + $Ca(OH)_2$ + $CaCO_3$

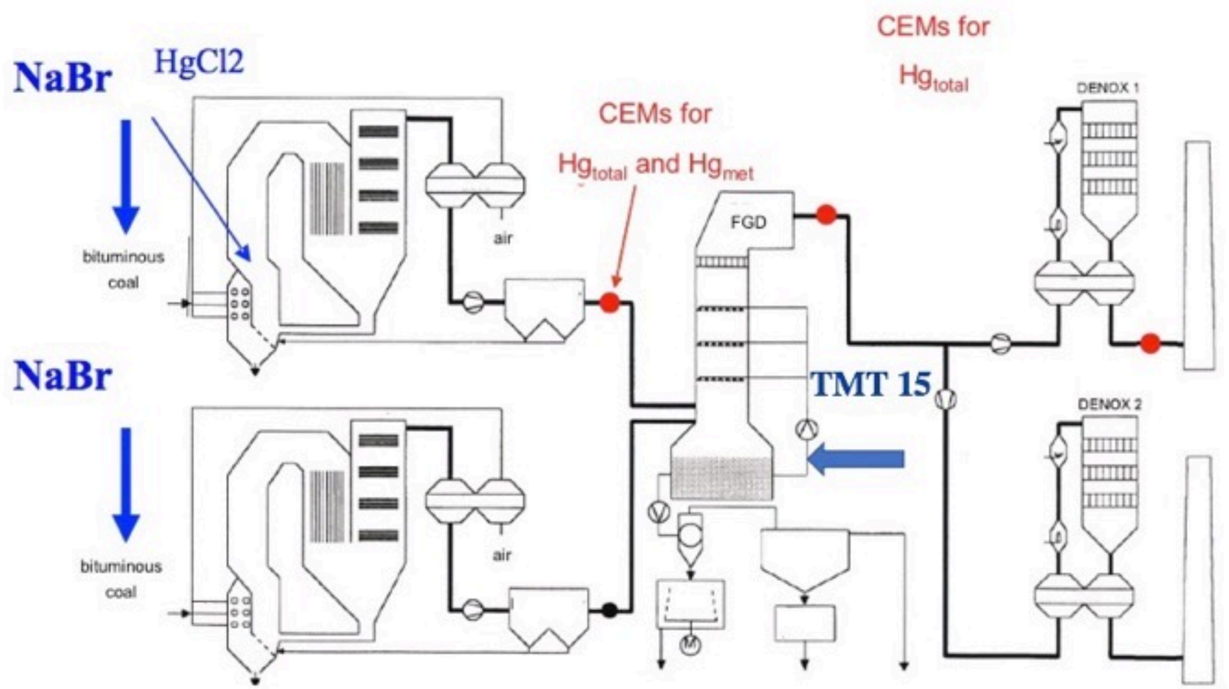
$CaBr_2$



Chlorinated Liquid Waste

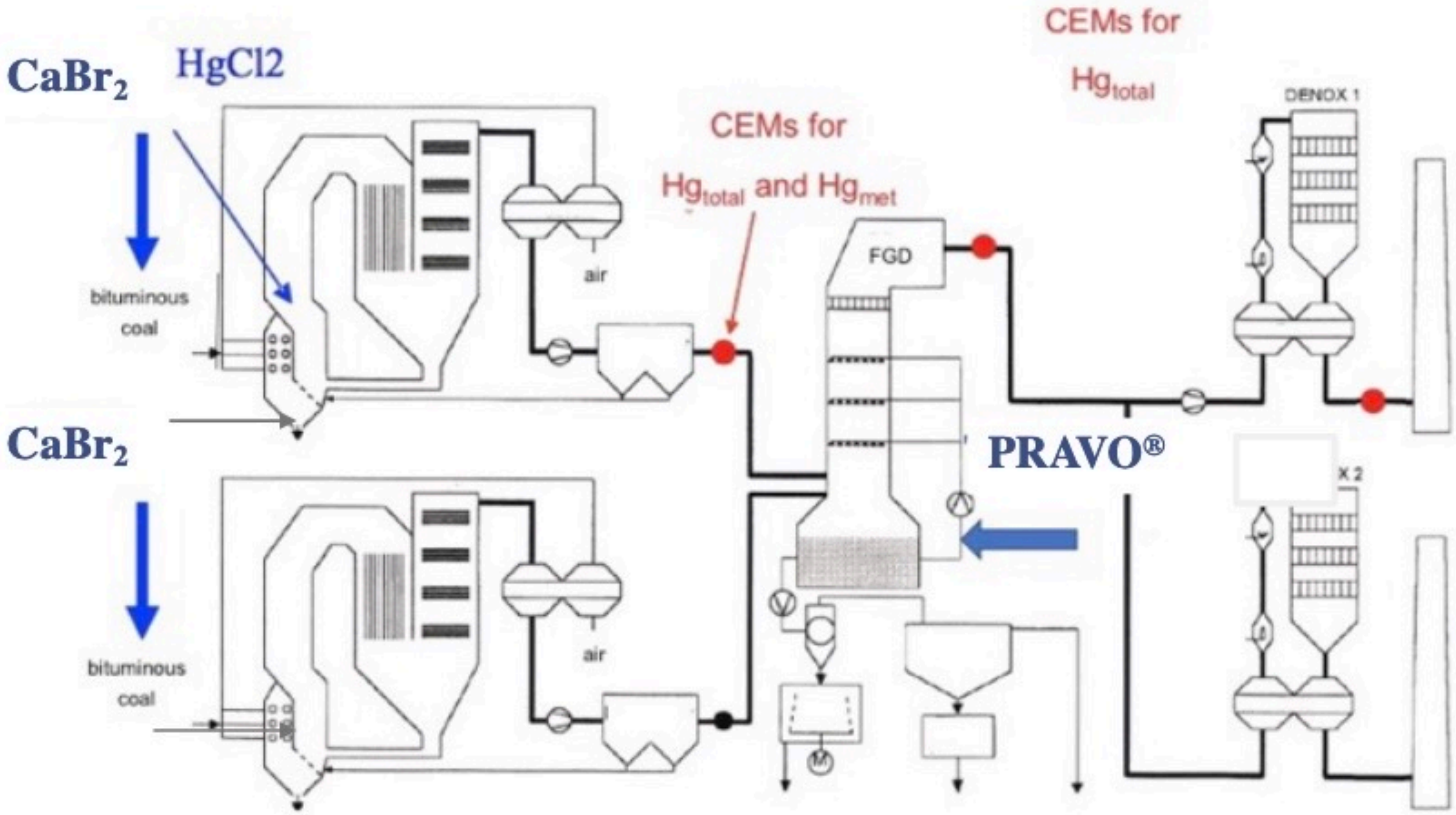
(Dichlorpropan, 75 % Cl)

Industrial Tests in Germany by BAYER AG at PC-fired Wet Bottom Boiler with Tail-End SCR injecting NaBr-Solution and TMT15 in 2001 and 2002



Pre-combustion bromide addition onto the fired coal respectively in the hot fire-box
in 2002 at the Industrial Power Plant N230 of CURRENTA GmbH & Co OHG in Uerdingen

Industrial Tests in Germany by BAYER AG at PC-fired Wet Bottom Boiler with Tail-End SCR injecting $CaBr_2$-Solution and PRAVO®100 in 2008



Pre-combustion calcium bromide addition onto the fired coal

in 2008 at the Industrial Power Plant N230 of CURRENTA GmbH & Co OHG in Uerdingen

CURRENTA

VOSTEEN Consulting

High bromide dosage induces elevated Hgion-emission from tail-end SCR

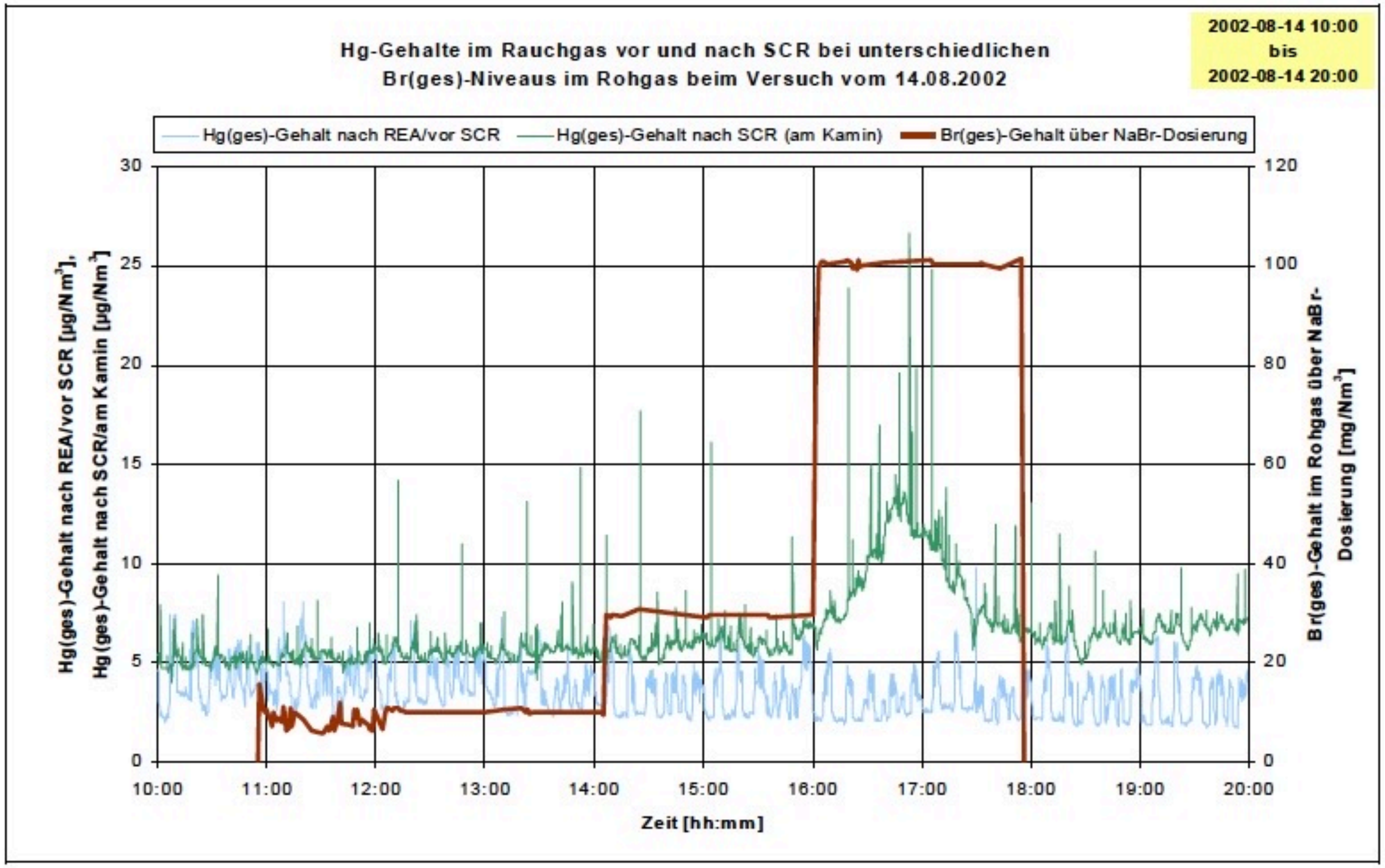


Abb. 5.21: Zeitlicher Verlauf der gemessenen Hg(ges)-Gehalte vor und nach SCR (am Kamin) bei unterschiedlichen Br(ges)-Niveaus im Rohgas beim Versuch vom 14.08.2002

BEMO-Technology combined with DeNOx-Technology

The precipitation agents of PAN Chemie Dr. Fülöp and Vosteen Consulting are

Precipan, PRAVO®100, PRAVO®200

These are inorganic liquid agents containing polysulfides and thiosulfate.

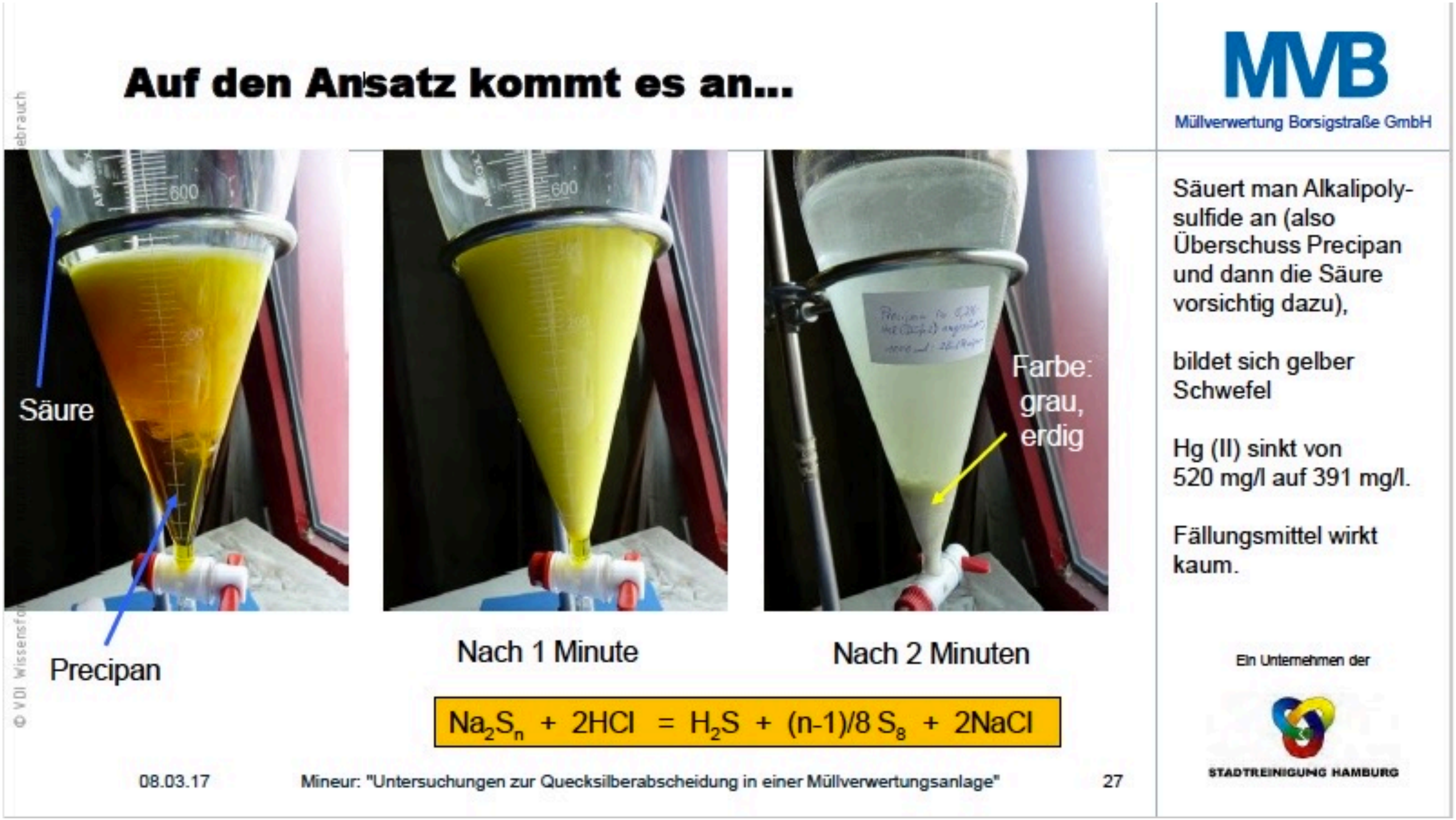
The highest content of active sulfur has PRAVO®200.

For mercury precipitation at wet FGD, only small injection rates are needed (e.g. < 1 liter /hour PRAVO® at 120.000 Nm^3/h flue gas)

An important initial step in such applications is the
Formation of highly reactive polysulfanes as H-S-S-S-S-H
by PRAVO® addition directly to the acidic milieu
as performed since 2008 at 3 MSWI lines of ENTEGA/HSE in Darmstadt

PRAVO® does work effectively also in the neutral or basical scrubber stage as performed since 2007/8 at 2 Fluidized Bed Incinerator lines for sewage sludge combustion at WWTP Karlsruhe –Neureuth

Tests in 2017 by Dr. Mineur from MVB, Hamburg: WRONG HANDLING



Tests in 2017 by Dr. Mineur from MVB, Hamburg: CORRECT HANDLING

Auf den Ansatz kommt es an…

$Na_2S_n + 2HCl = H_2S_n + 2NaCl$

MVB
Müllverwertung Borsigstraße GmbH

Lässt man umgekehrt die Lösung des Polysulfides im Schuss zu überschüssiger Säure fließen,

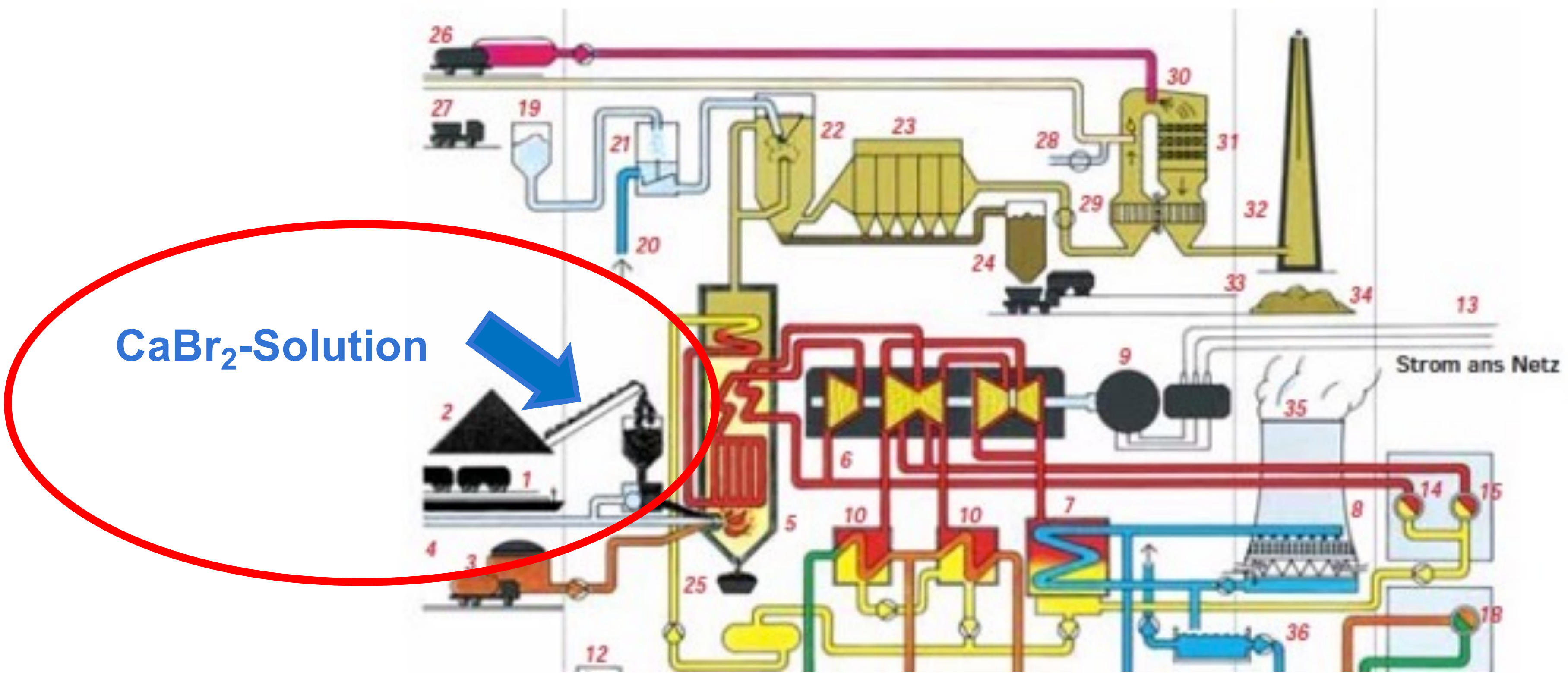
bildet sich eine Milch („Rohöl“ genannt).

Hg (II) sinkt von 520 mg/l auf 0,51 mg/l.

Fällungsmittel wirkt praktisch vollständig.

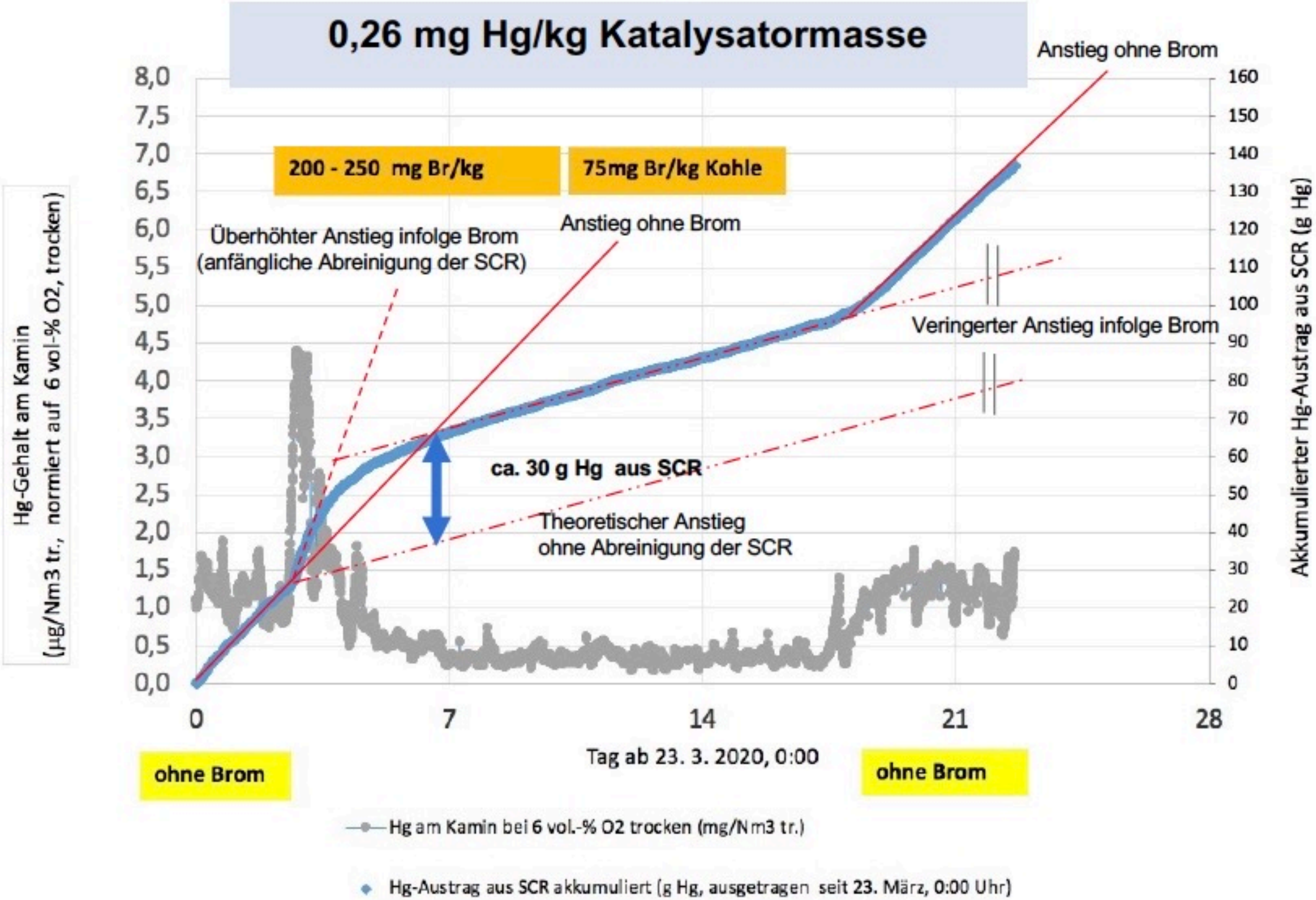
Ein Unternehmen der STADTREINIGUNG HAMBURG

Industrial Tests in 2020 (Germany) at a small PC-fired Boiler with Tail-End SCR adding $CaBr_2$-Solution onto the coal



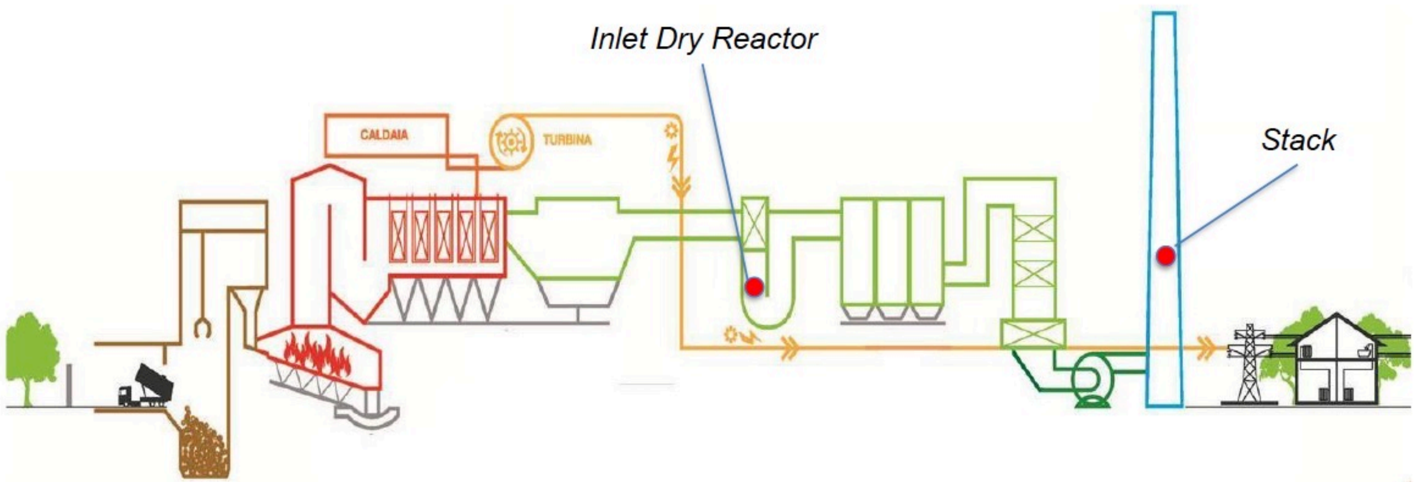
Injecting CaBr2-Solution allows for 0.5 mg Hg/Nm³ dry (6 %O_2) at stack

Hg-Purging of the Tail-End-SCR Catalyst
when starting Bromide Addition onto the coal (see peak)



Torino Waste to Energy Plant combining Dry APC with tail-end SCR

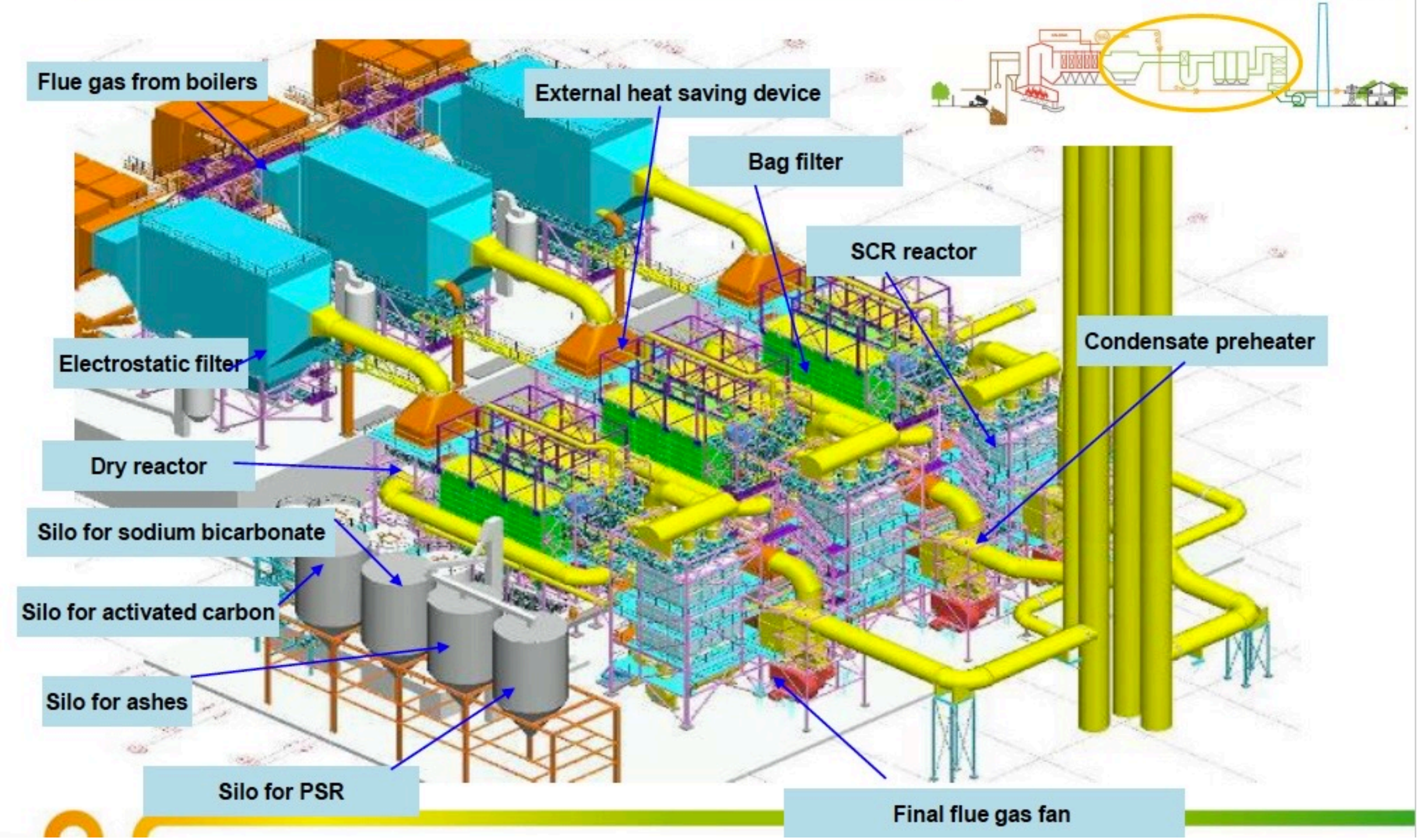
Hg instrumentation - current configuration



Each line has been equipped with the following instrumentation for the mercury continuous measurement:

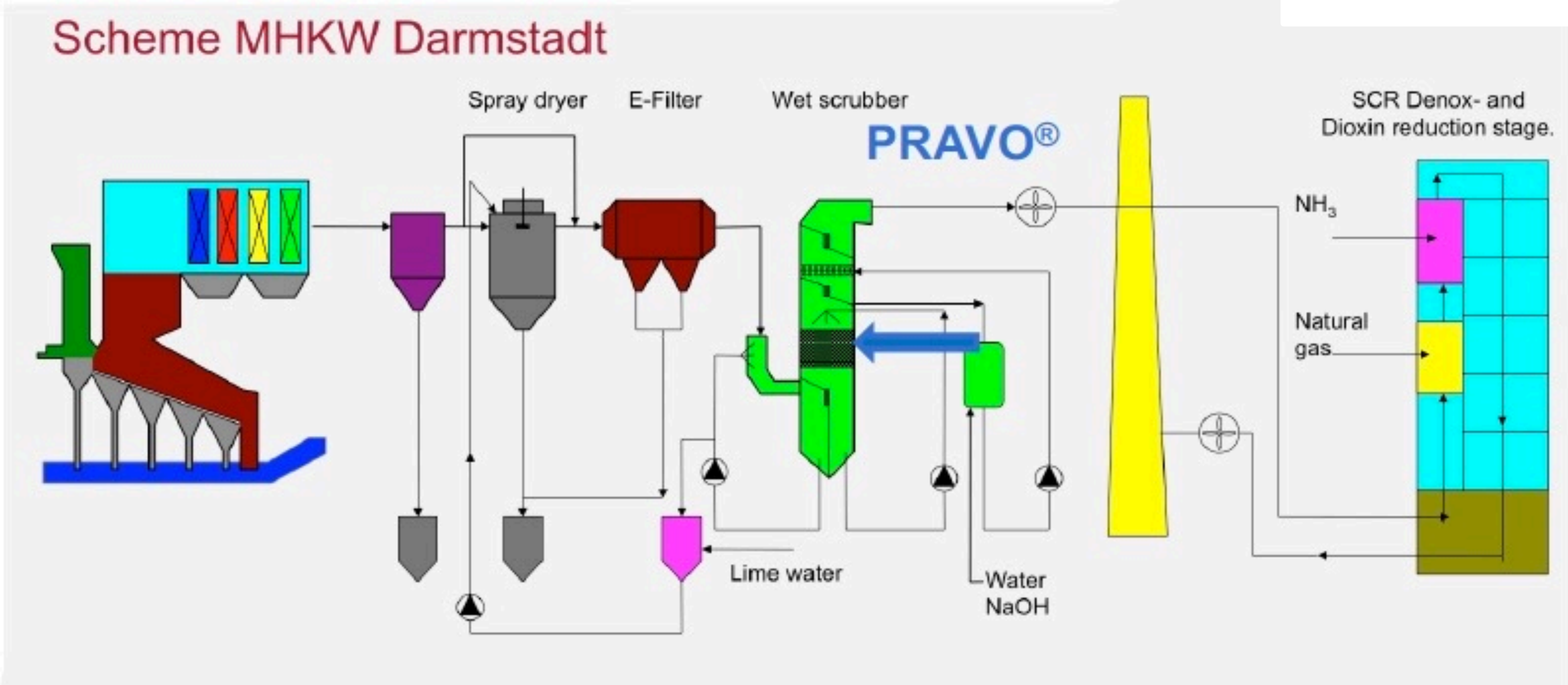
- Boiler outlet (before activated carbon injection) :
  - analyzer with thermocatalytic reactor;
  - analyzer with high-temperature Hg converter;
- Chimney – analyzer with thermocatalytic reactor.

The flue gas cleaning system (3D)



BEMO-Technology combined with DeNOx-Technology

Tests in 2008 (Dipl.-Ing. Mielke)



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License granted in 2008 to WE Power Station Pleasant Prairie (2 x 600 MWe Units with SCR, ESP, WFGD, in commercial opperation since January 1st, 2010)

2 x 600 MWel
Base Load
(24 hours/day)

PRB coal
2 x 315 tons/hour
0.11 ppm Hg

KNX (as $CaBr_2$)
25 ppm Br on coal

Hg_{total} at stack
< 1 µg/dscm
(both units)

ALSTOM

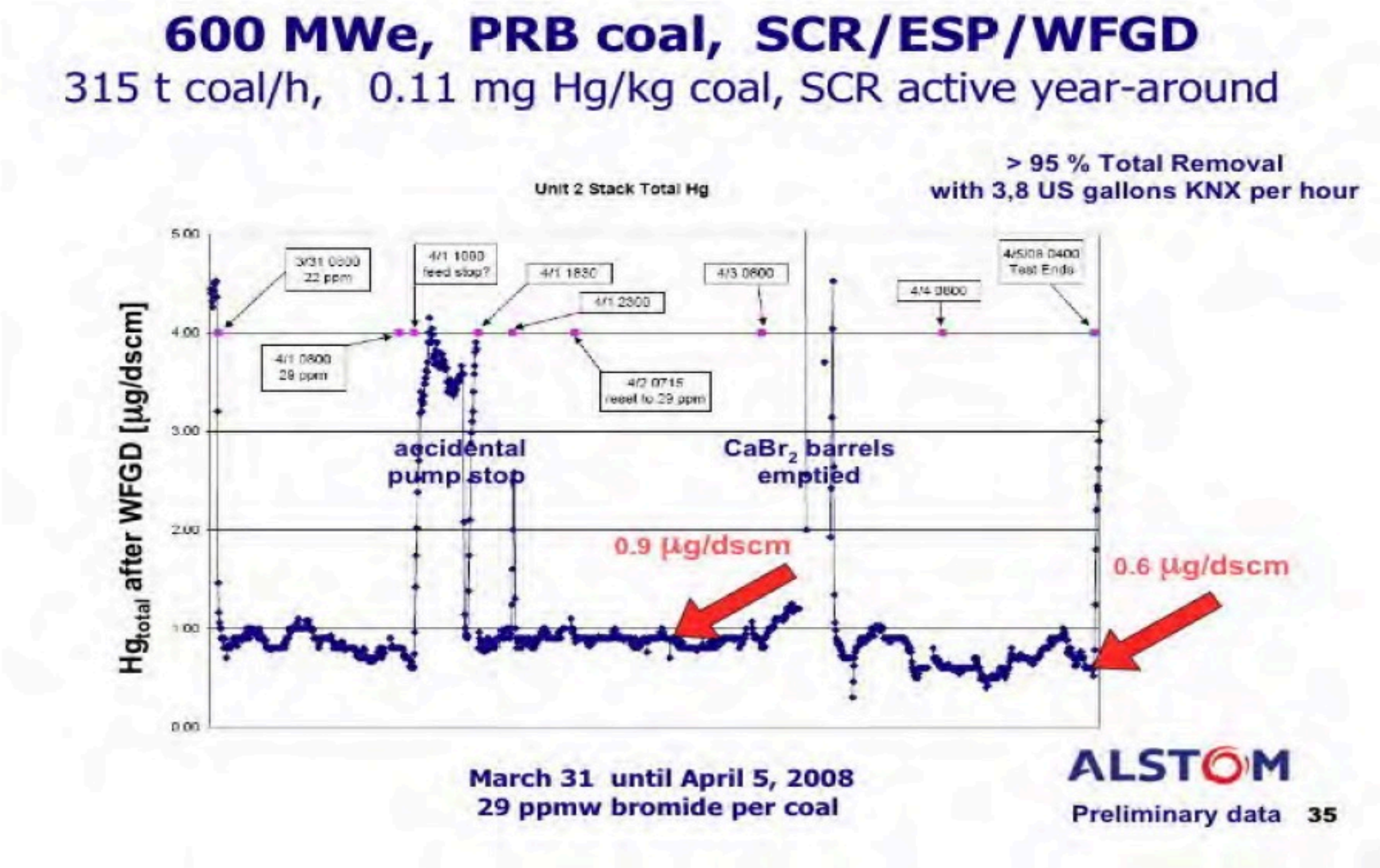


Figure 18b:
Very first test results applying the BEMO-technology
at WE Peasant Prairie in March and April 2008

Calcium Bromide Injection

- All Testing conducted @ Miller Unit 4 (4x700 MW)
- Inject $CaBr_2$ onto coal (equivalent Bromide per coal: 0 ppm – 350 ppm)
- Three Phases
    - Phase I: Measurement Only
    - Phase II: Pilot FGD removal
    - Phase III: 90 Days (full-scale)
    - 2006; 2008 & 2010
- Hg Oxidation w & w/o SCR
- Verify Removal via FGD
- Balance of Plant Impacts

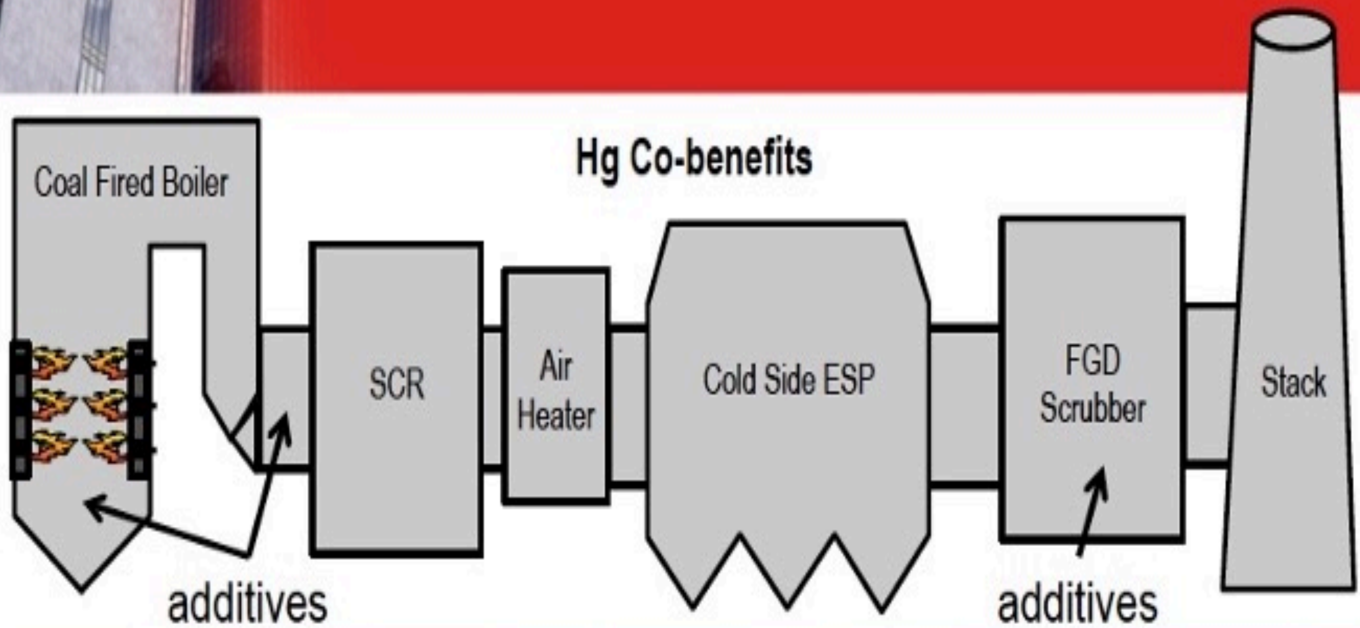
Alabama Power Company
J.H. Miller Station Units 1, 2, 3 and 4

Figure 14:

Alabama Power's J.H. Miller Station

Units 1, 2, 3 and 4

Calcium Bromide Injection



Alabama Power Company
J.H. Miller Station Units 1, 2, 3 and 4

Miller Average Elemental Mercury Concentrations
Measured During Each Bromide Injection Test (October 2006)

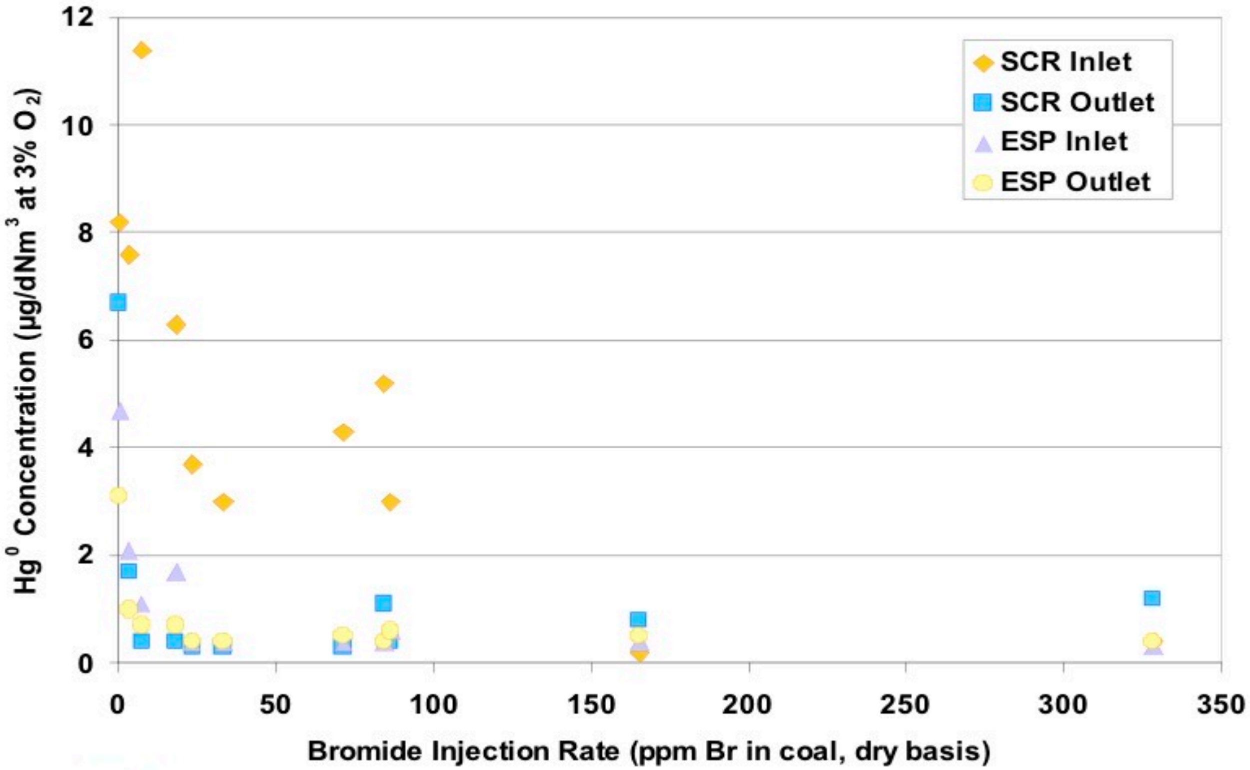


Figure 15:
Hg(0) concentrations at the SCR Inlet and SCR Outlet
as well as at the ESP Inlet and ESP Outlet

Phase III: Full Scale Testing

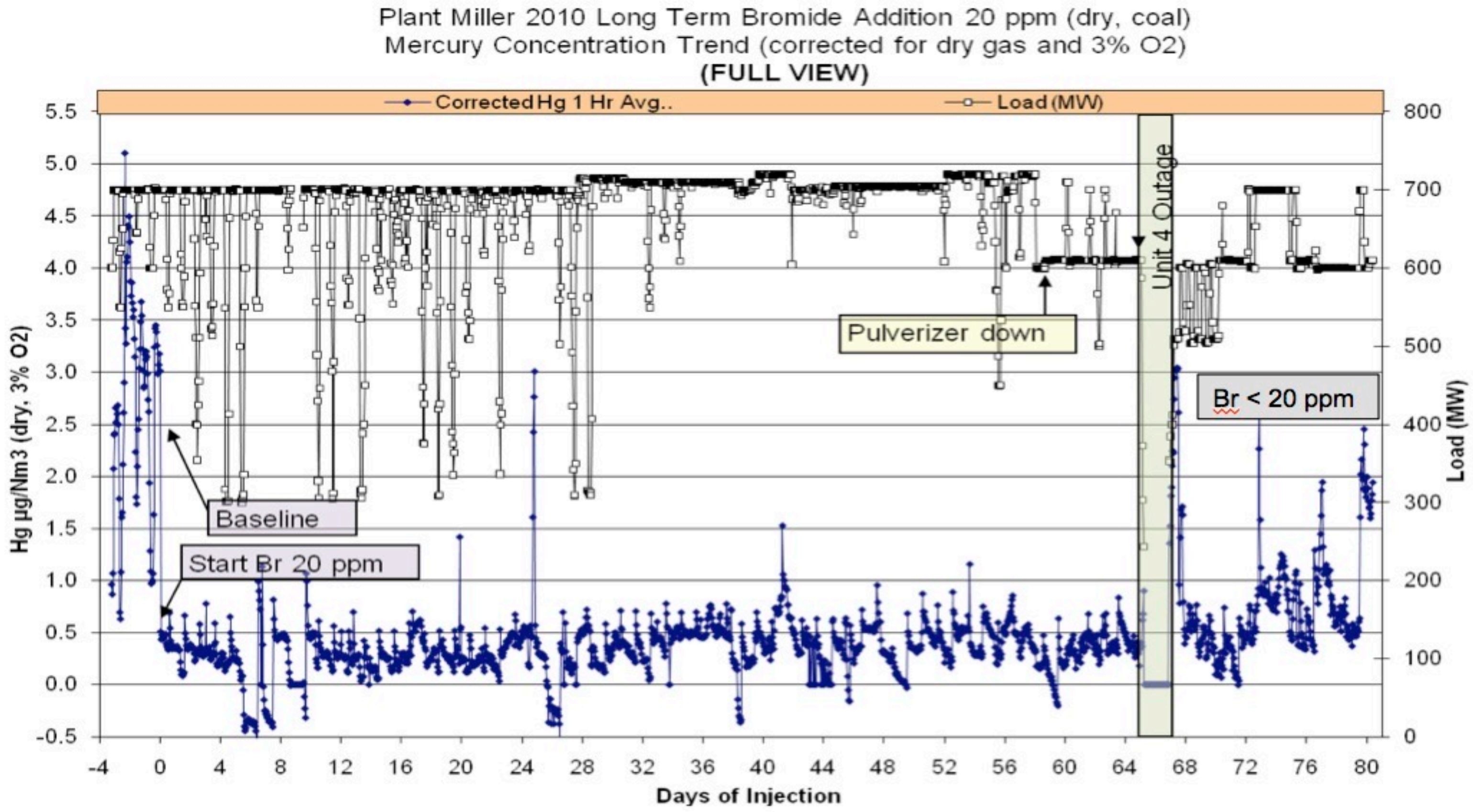


Figure 16:

Hg-concentrations at stack

during final long-time test (72 days @ 24 h/d) under 20 ppmw Br per dry coal

Stadtwerke München
Kraftwerk Nord, Block 2

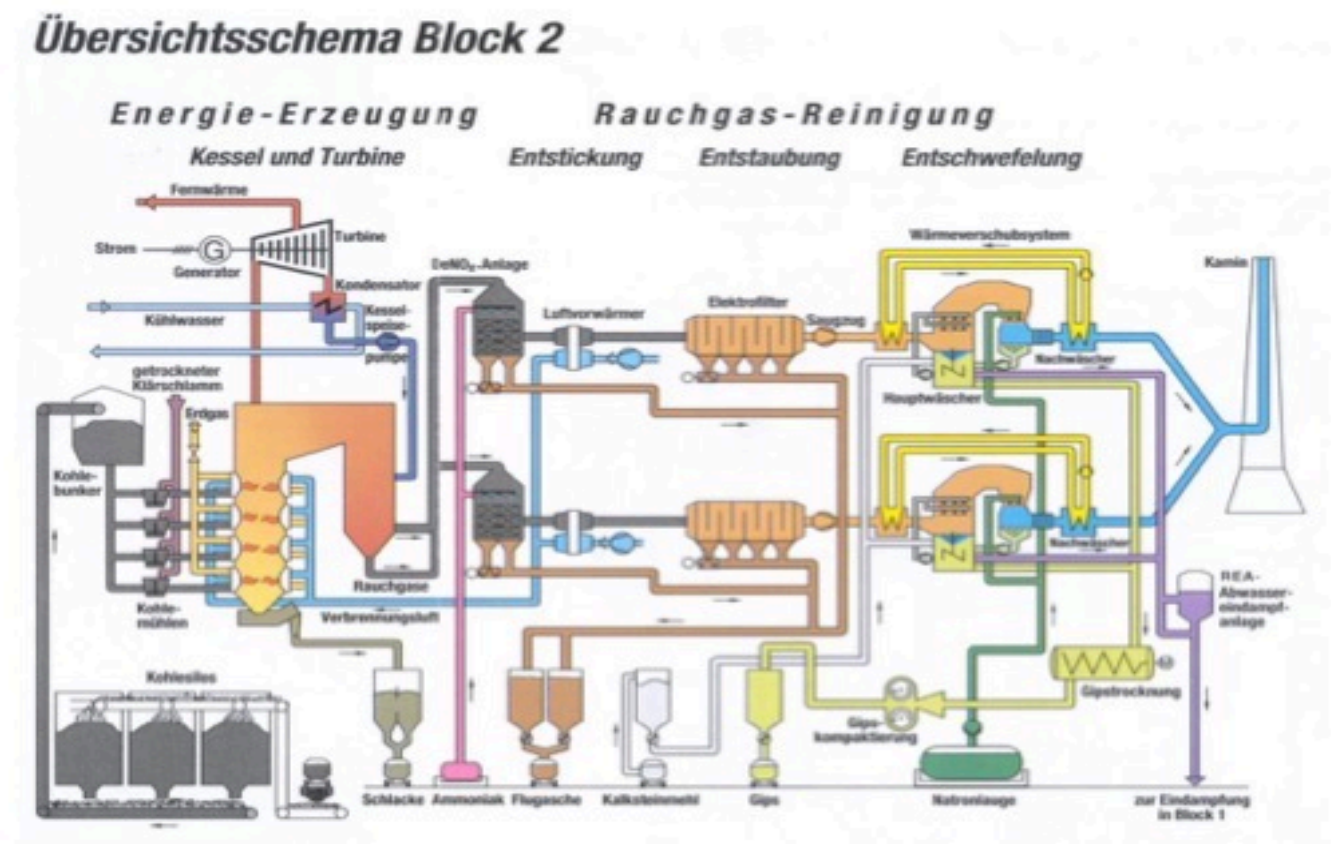


Figure 24:

Unit 2 of Stadtwerke München (SWM)

in Munich-North (Unterföhring)

1000 l IBC at Stadtwerke Munich, Unit 2, for its 2 wet FGD for PRAVO®200 under commercial application since 2016

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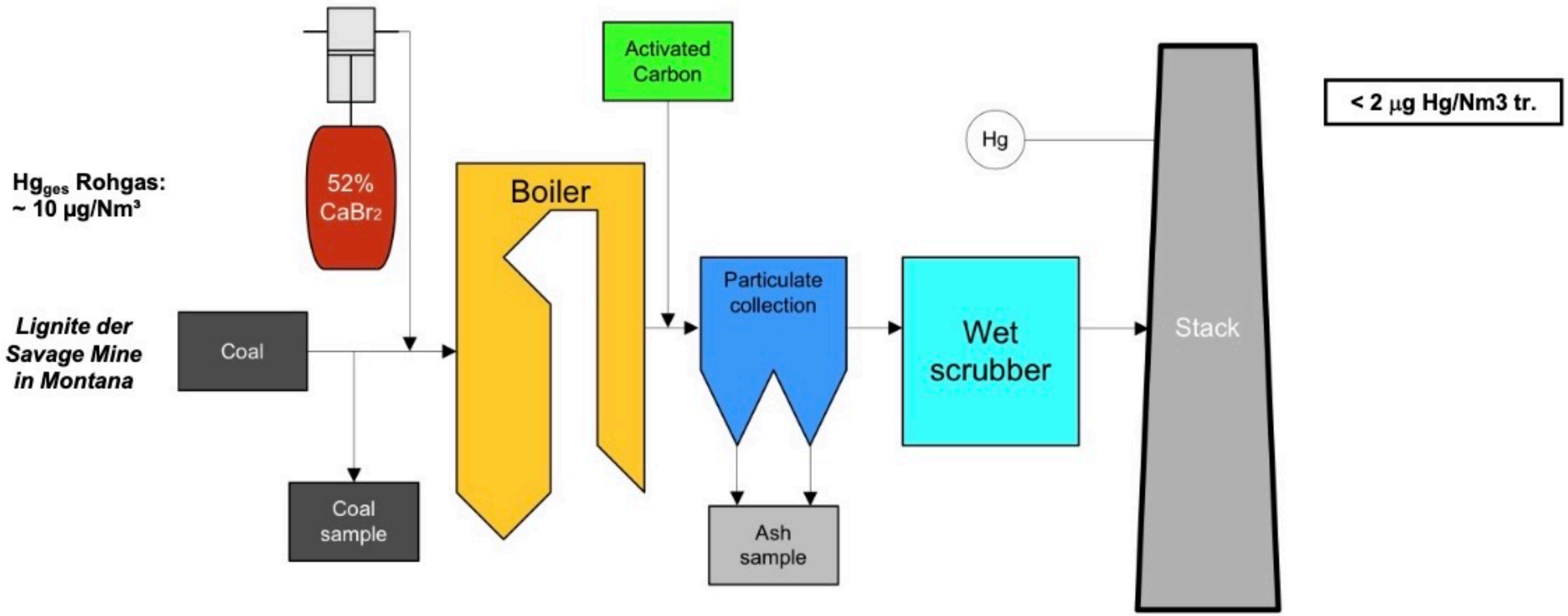
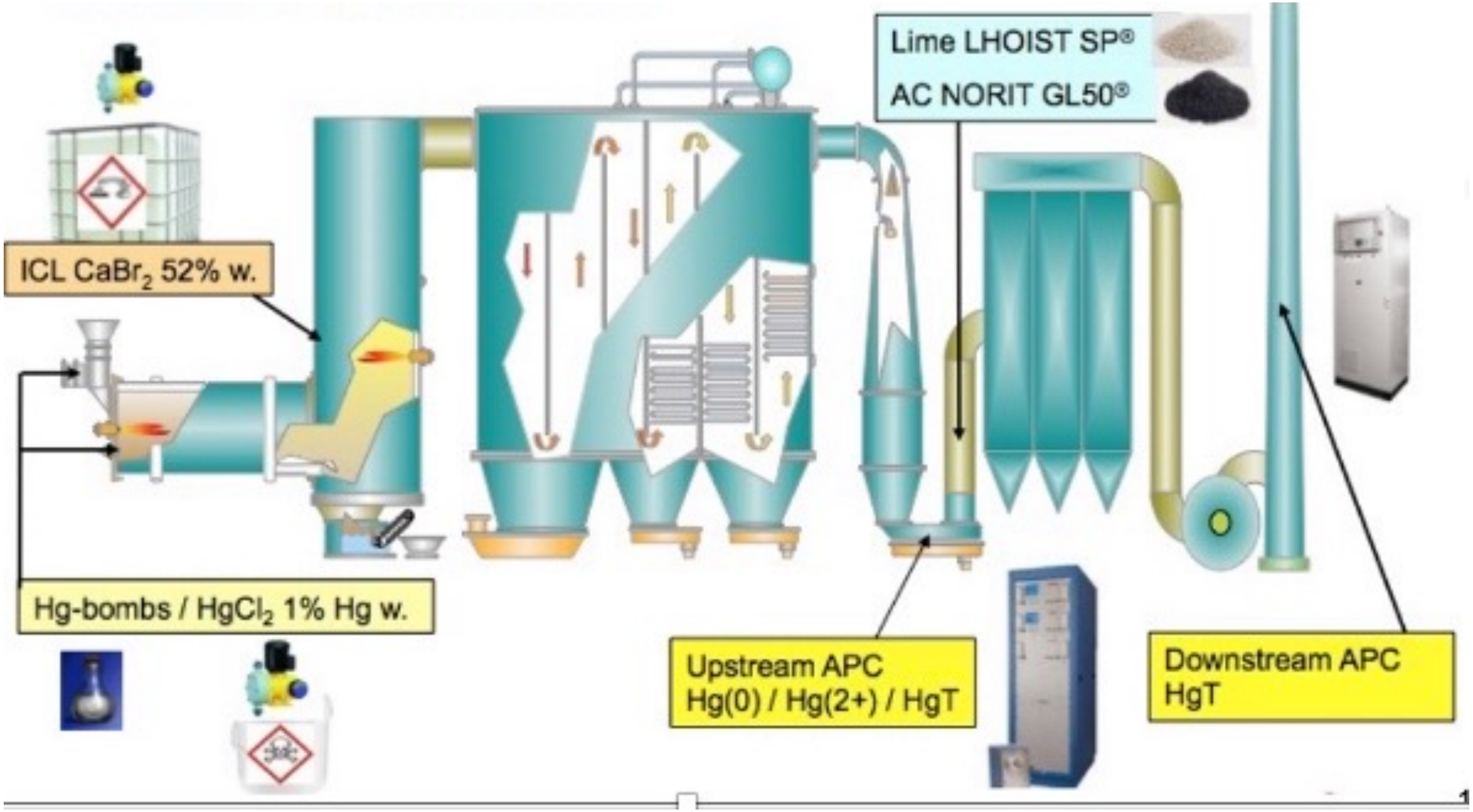
LIGNITE-FIRED PPOWER PLANT MDU LEWIS & CLARK
(near Sidney, Montana in USA)

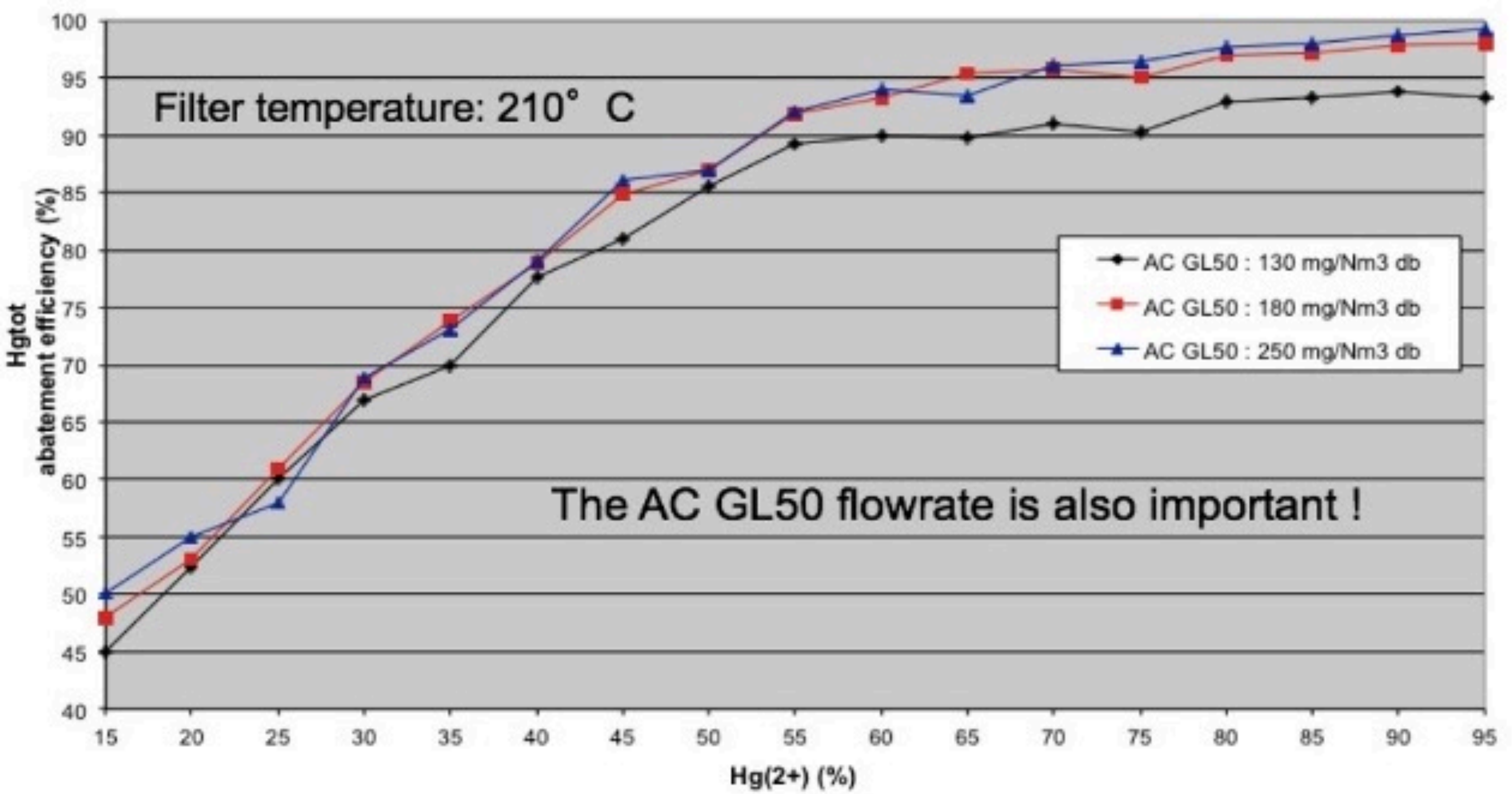
PRECOMBUSTION BROMIDE ADDITION COMBINED WITH INJECTION OF NORMAL PAC SINCE JANUARY 2010



Hazardous Waste Incineration Plant with SNCR and dry APC Operated with $CaBr_2$-Solution since 2016 (France)



Mercury oxidation upstream of dry APC improves sorptive Hg capture at normal (undonated) AC towards 100 %



Braunkohle gefeuerter Kraftwerksblock

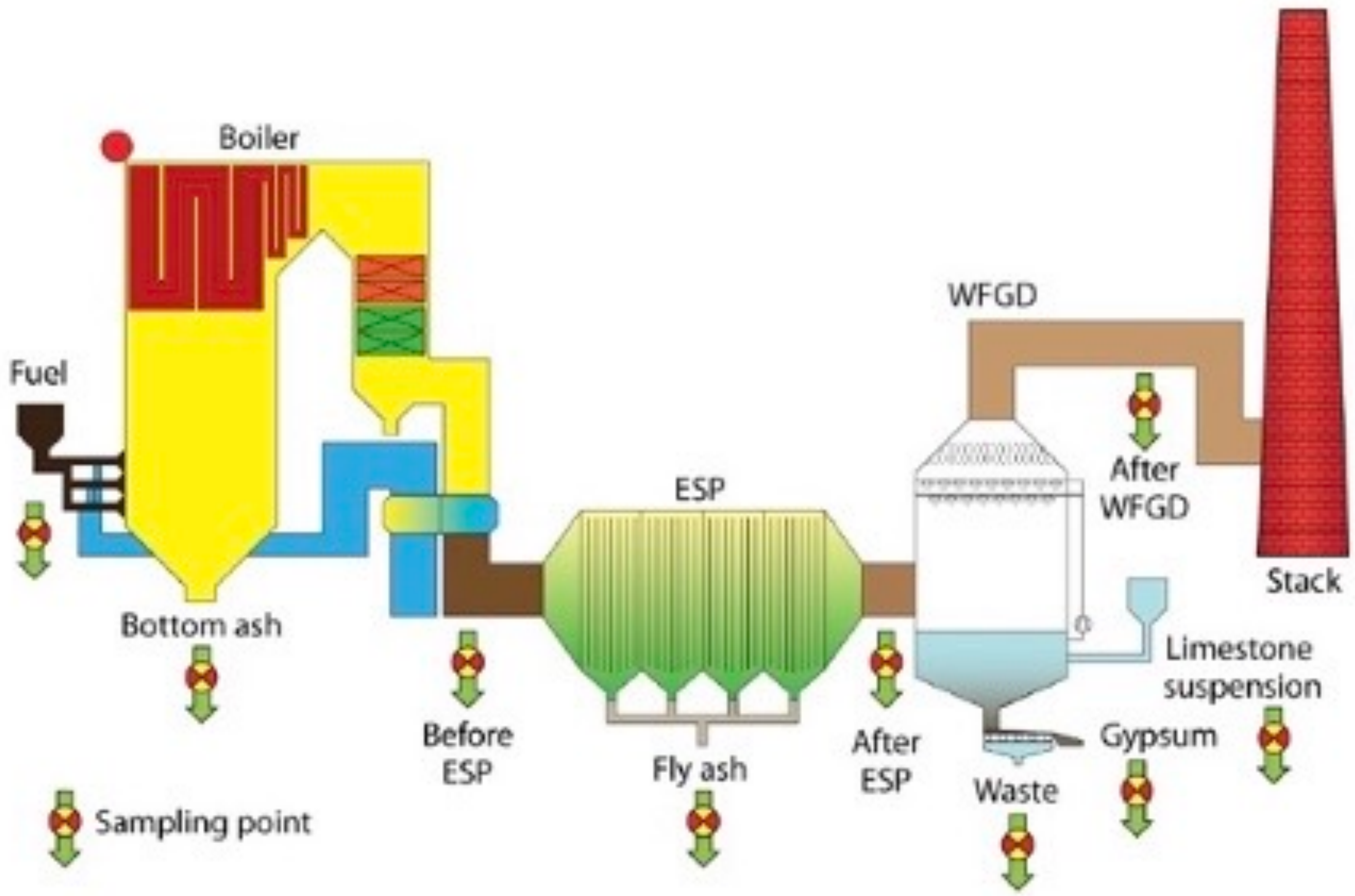


Fig. 2. Schematic diagram of the sampling campaigns in the sampled power plants.

Górnictwo i Energetyka Konwencjonalna S.A.

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PGE's Lignite-Fired Power Plants in Belchatów (in total 5100 MWe):

All operating Units 2-12 and the new Unit 14 as well are served with Bromide (Status 2022)

Unit 14 | Units 12 – 7 | Units 6 – 2

Widok z lotu ptaka na Elektrownię Bełchatów

PGE‘s Lignite-Fired Power Plants in Turów (in total 2000 MWe):

All operating Units (except the new Unit at right hand side) are served with Bromide (Status 2022)

Conclusions

The cost-effective BEMO-Technology – i.e. mercury abatement by small amounts of bromide as coal additive and PRAVO® as scrubber additive – is a well established and highly successful technology for power plants and WtE-plants with and without SCR-DeNOx-Systems of any kind.

Incomplete mercury oxidation induces accumulation of residual elemental mercury Hg° at catalysts in tail-end SCRs, but not in high dust SCRs with its immediate mercury release as oxidized Hg_{ox}, governed by the upstream of APC system still available halogens.

Complete mercury oxidation and therewith optimal mercury abatement attaining mercury removal rates well above 95 % also at lignite-fired plants without SCR system, but with or without SNCR system needs limited air staging, to provide always sufficient residual oxigen in the overfire-temperature range enabling the formation of free bromine Br_2 via the bromine-Deacon reaction. An indicator of a lack of oxigen can be the formation of CO.