54th POWER PLANT COLLOQUIUM
at October 18th and 19th, 2022
International Congress Center Dresden

Bromine-Enhanced Mercury Oxidation at the PGE GiEK Lignite Fired Power Plant Bełchatów (Poland)

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Bełchatów, Polen

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

Agenda

PGE's Lignite-Fired Power Plants in Belchatów (in total 5,100 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

380 MWe Units 2 -12
Rafako-Babcock design

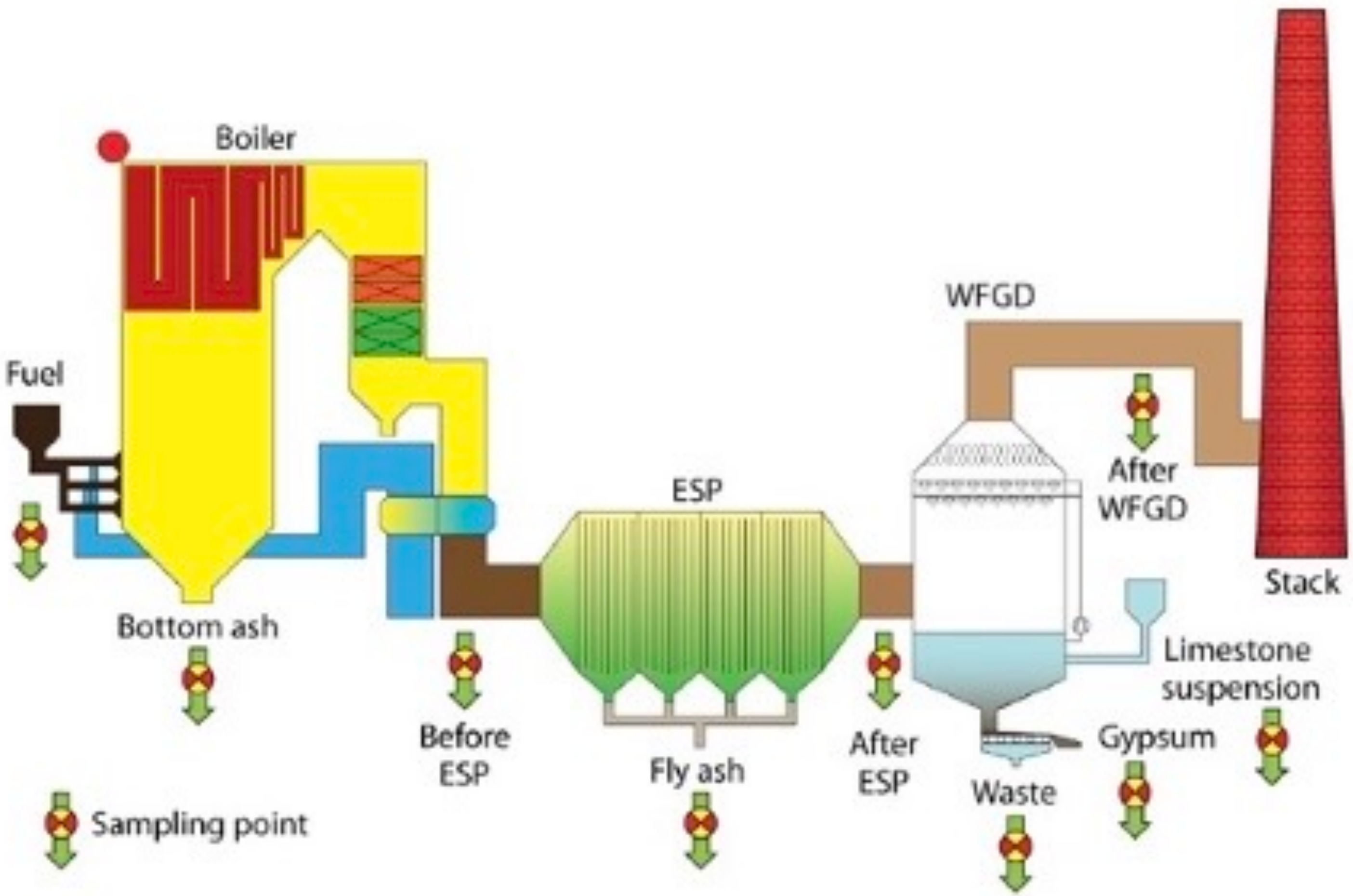
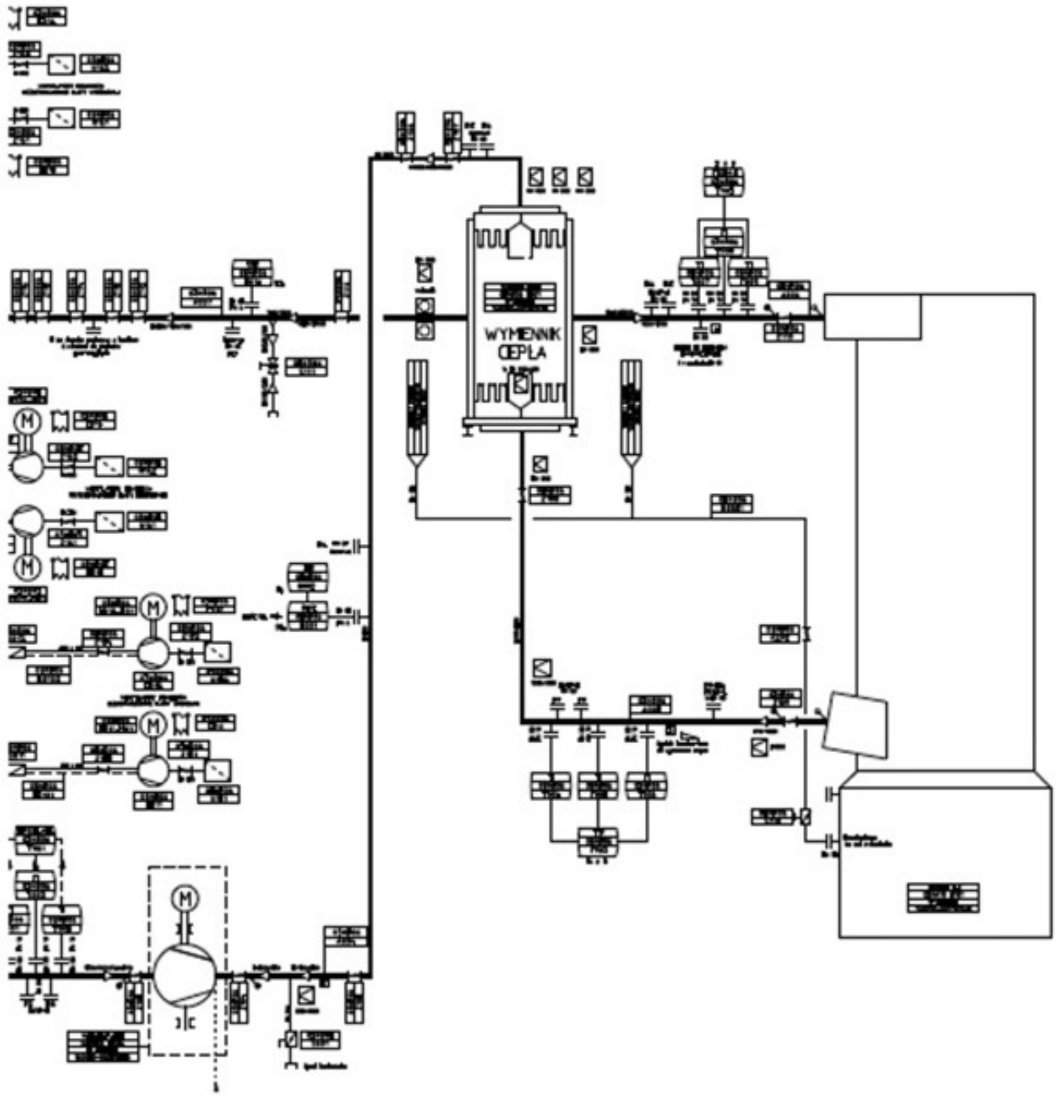


Fig. 2. Schematic diagram of the sampling campaigns in the sampled power plants.

Advantage Bełchatów :
There are no rotating REGAVOs



The cross-flow heat exchanger is perfect with respect to complete mercury removal („“no bypass of flue gas around the FGD, streaming from the FGD raw ras to the FGD clean gas“)

STEAG-Kraftwerk Ruhr operating with rotating ReGaVo:

Transfer of oxidized mercury Hg^{++}
from ESP-oulet to FGD-exit (clean gas)

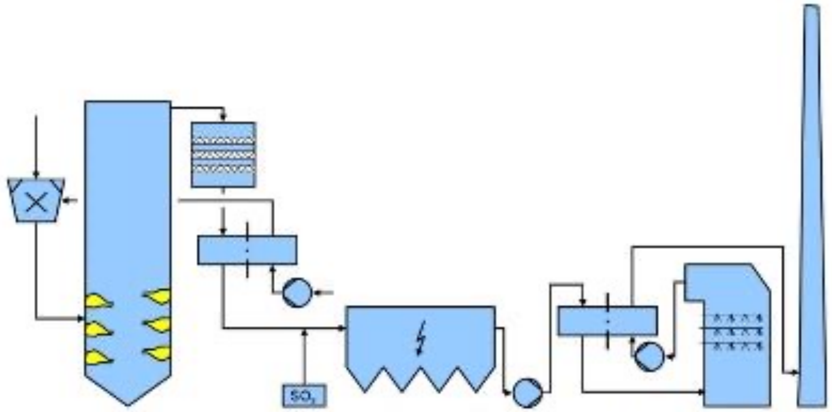


Bild AII-1. Anlagenschema Kraftwerk Ruhr: Rohrkugelmühlen, Trockenfeuerung (Boxer), High-Dust-DeNOx, LuVo, SO_3-Konditionierung, E-Filter, Saugzug, ReGaVo, REA, Nassgebläse, ReGaVo und trockener Schornstein.

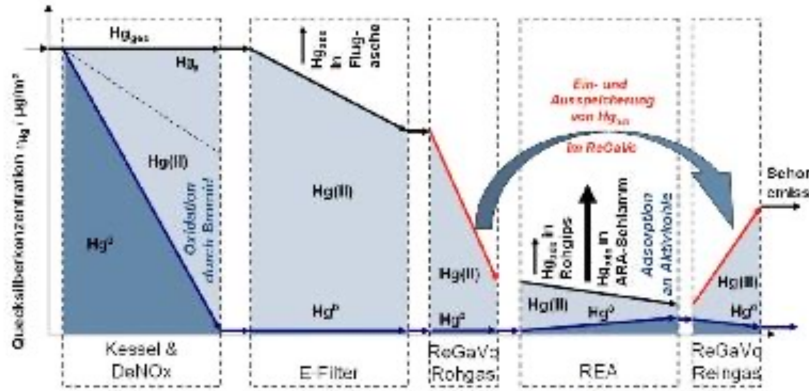


Bild 6-1. Vereinfachte Darstellung des Verlaufs der gasseitigen Hg-Speziierung im Kraftwerksprozess des Kraftwerks Ruhr (oder vergleichbar) bei Einsatz der diskutierten Verfahren

Source: Disssertation Riethmann (2013)

Block 14 with 858 MWe, built by Rafako-Alstom

netto el. efficiency of Unit 14: 41,5 %

APC at Unit 14 in Belchatów showing the FGD Lines 1 and 2 (from Google maps)

Continuous Mercury Monitoring Systems

CMM AutoQAL and CMM

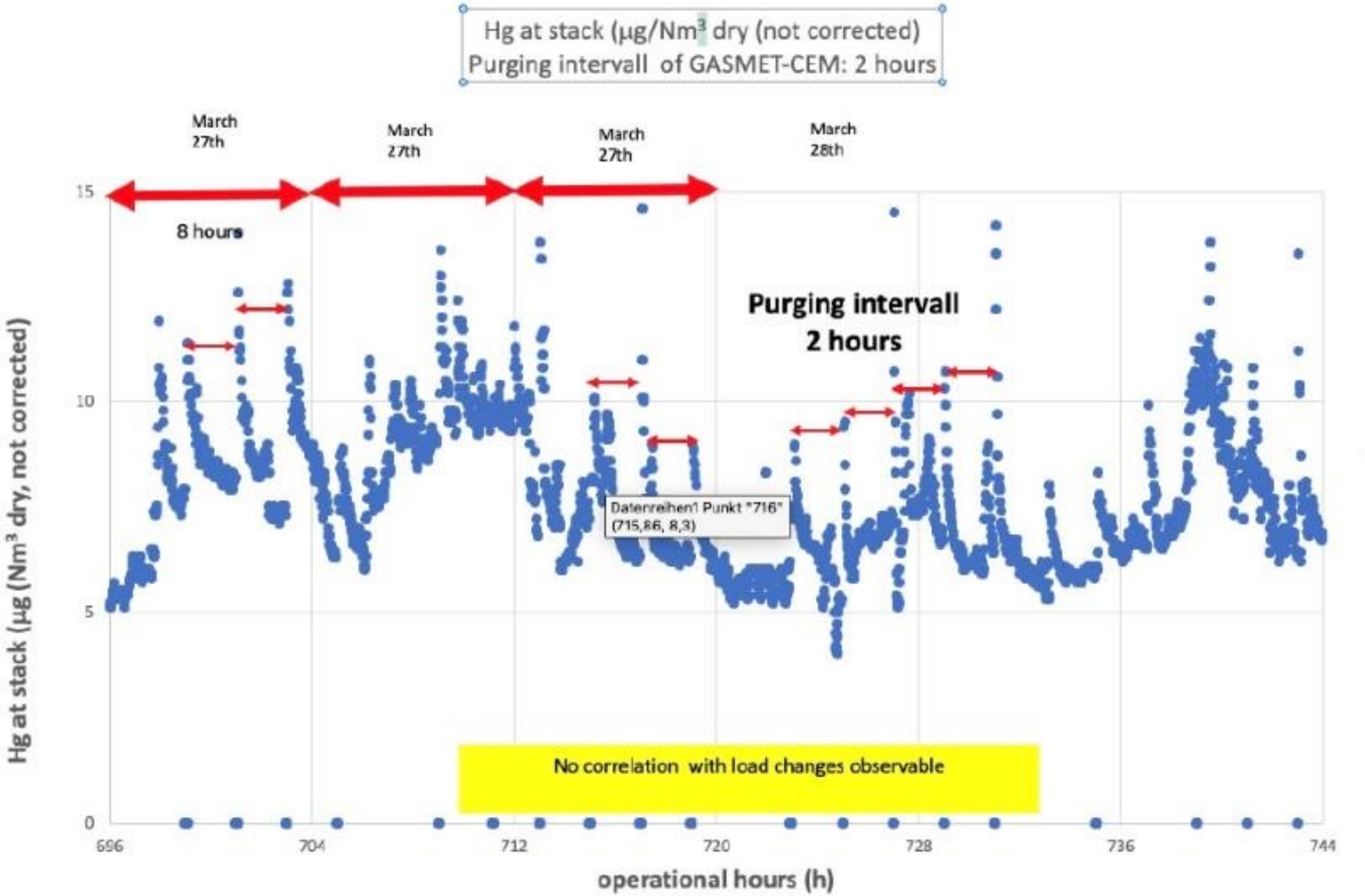
Gasmet offers two solutions for Continuous Mercury Monitoring, the CMM and CMM AutoQAL.

Both systems provide the highest sensitivity and annual availability on the market. CMM AutoQAL is the only TÜV and MCERTS certified solution with automatic and truly integrated QAL3 validation tool. Systems offer certified measurement with the lowest certified range in the world (0-5 µg/m3). The highest certified measurement range of the system is 1000 µg/m3 and even higher concentration peaks can be measured without any hardware changes. CMM has both TÜV and MCERTS (QAL1) certificates.

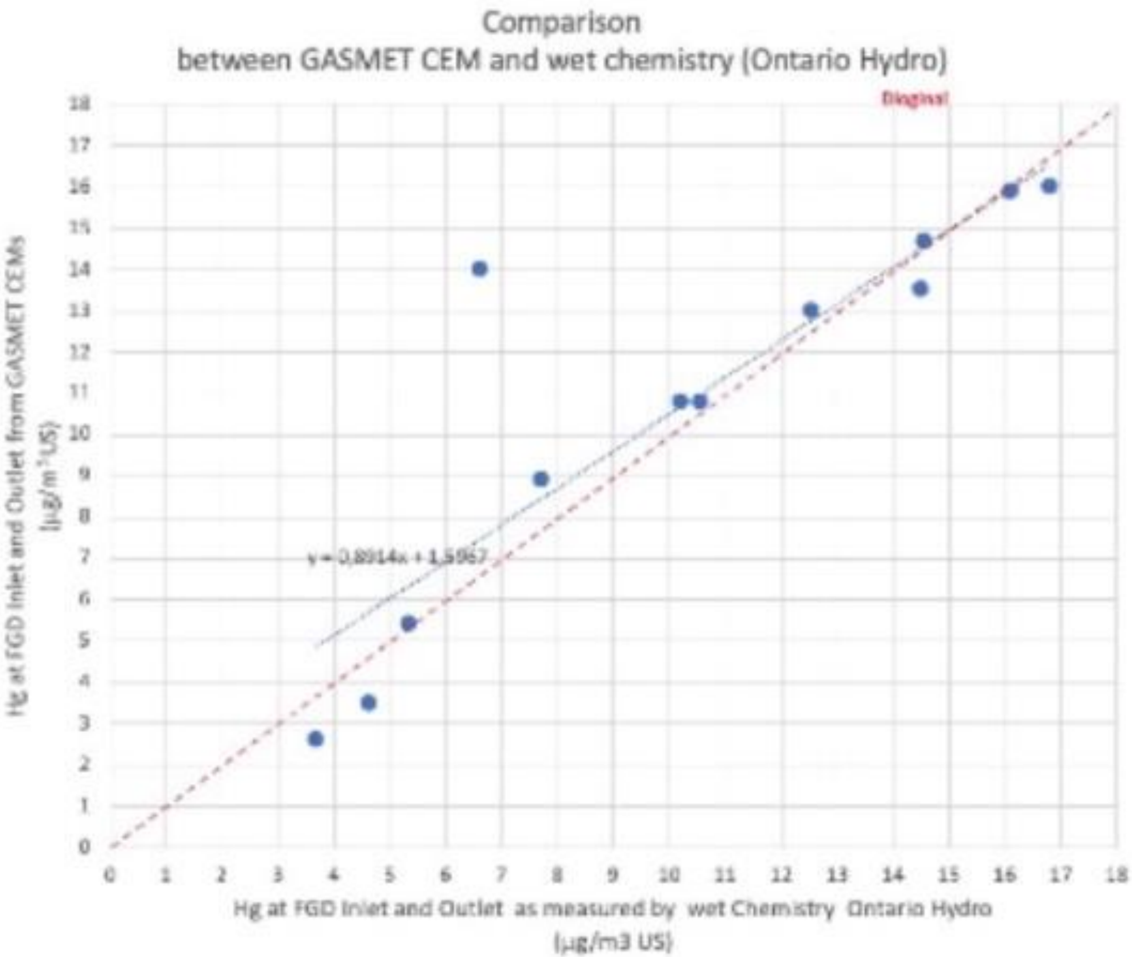
CMM AutoQAL and CMM both consist of:

- Dilution probe
- Heated sample line
- Mercury analyzer
- Test gas generator

Gasmet mercury analyzer is based on **Cold Vapor Atomic Fluorescence (CVAF) measurement principle,** which gives the highest sensitivity in the world. The system is fully automatic, and the automatic calibrations are done by user-defined intervals. CMM AutoQAL has an integrated and certified test gas generator with possibility to do both Hg0 and HgCl2 checks means that there is no longer a need for an external gas generator for QAL3 operations.


Hg at stack (µg/Nm³ dry (not corrected)
Purging intervall of GASMET-CEM: 2 hours
March 27th
March 27th
March 27th
March 28th
8 hours
Purging intervall
2 hours
Datenreihen1 Punkt "716"
(715,86, 8,3)
No correlation with load changes observable
Hg at stack (µg (Nm³ dry, not corrected)
operational hours (h)
0
5
10
15
696
704
712
720
728
736
744

Control of the GASMET CEM measurements by comparison with wet chemistry (Ontario Hydro) - should be extended especially for the Hg-levels < 5 µg/m³



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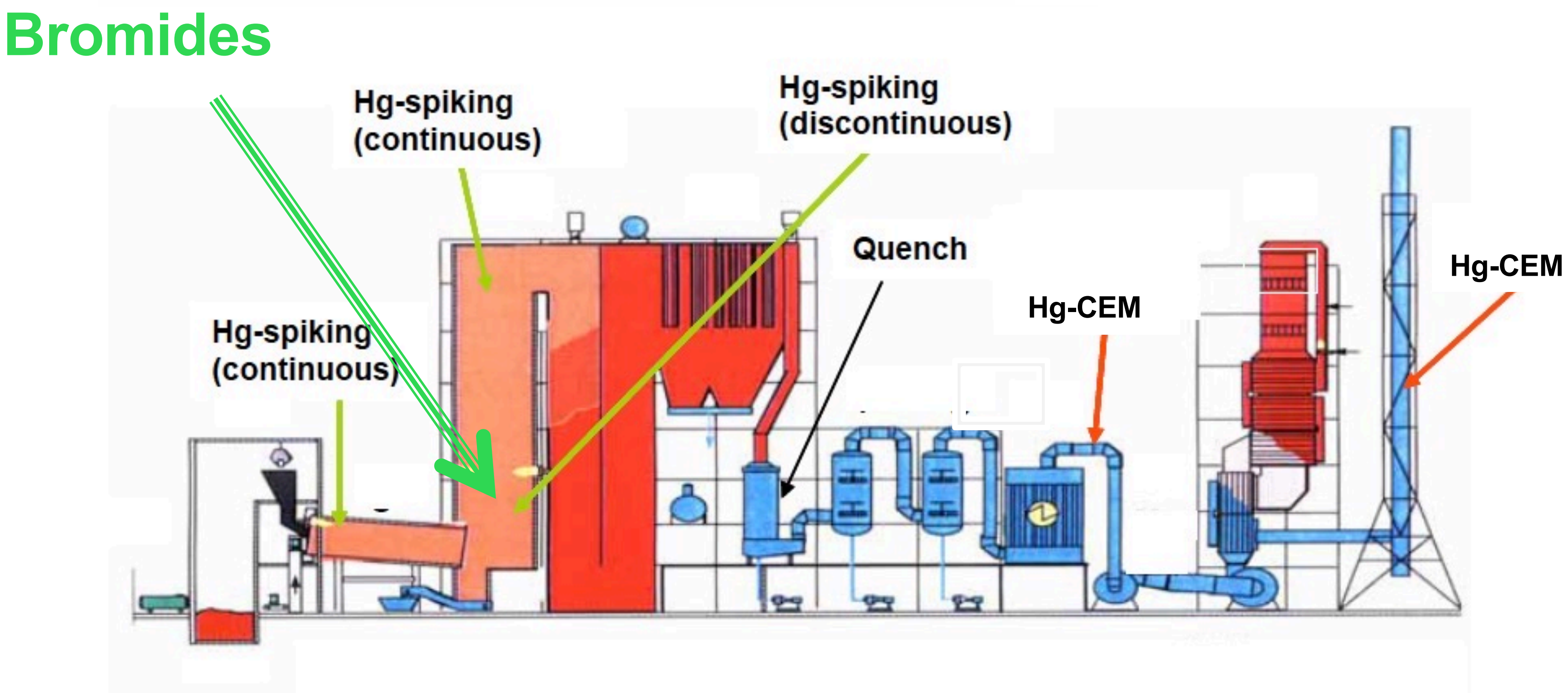
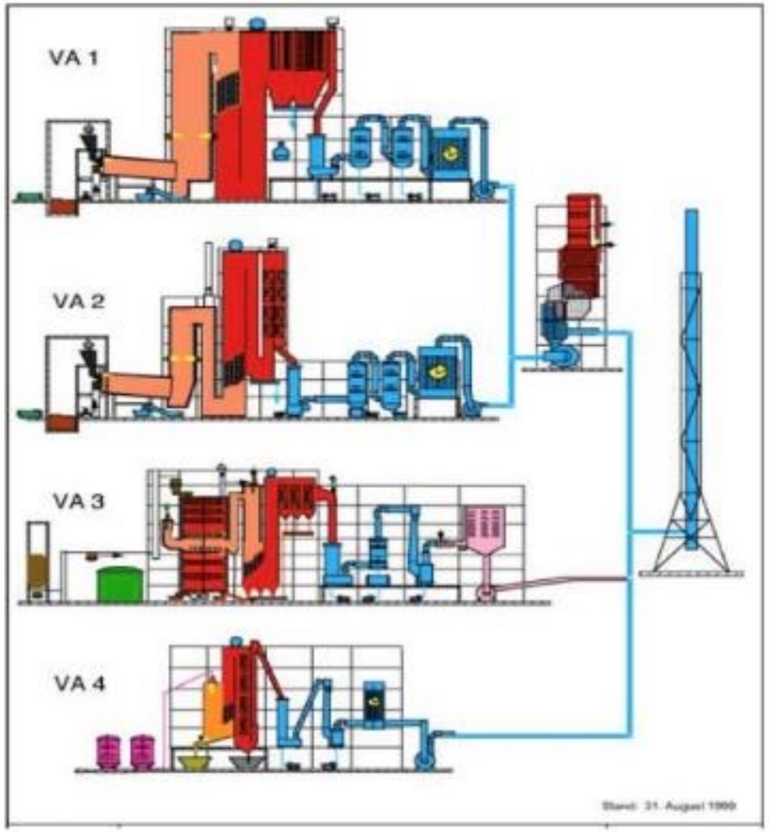
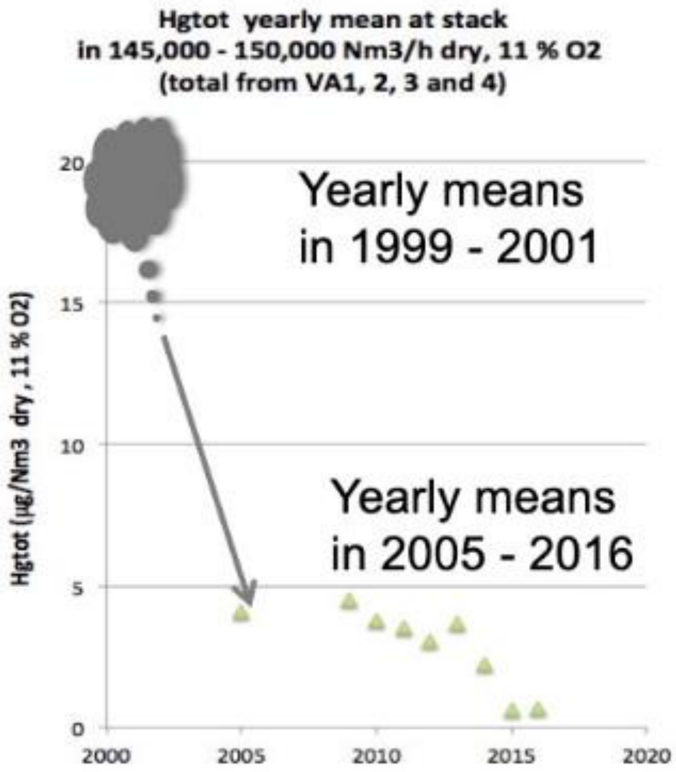
Bromides applied as Mercury Oxidizers by BAYER/CURRENTA since 2000

injecting bromide solutions (HBr, NaBr, $CaBr_2$)



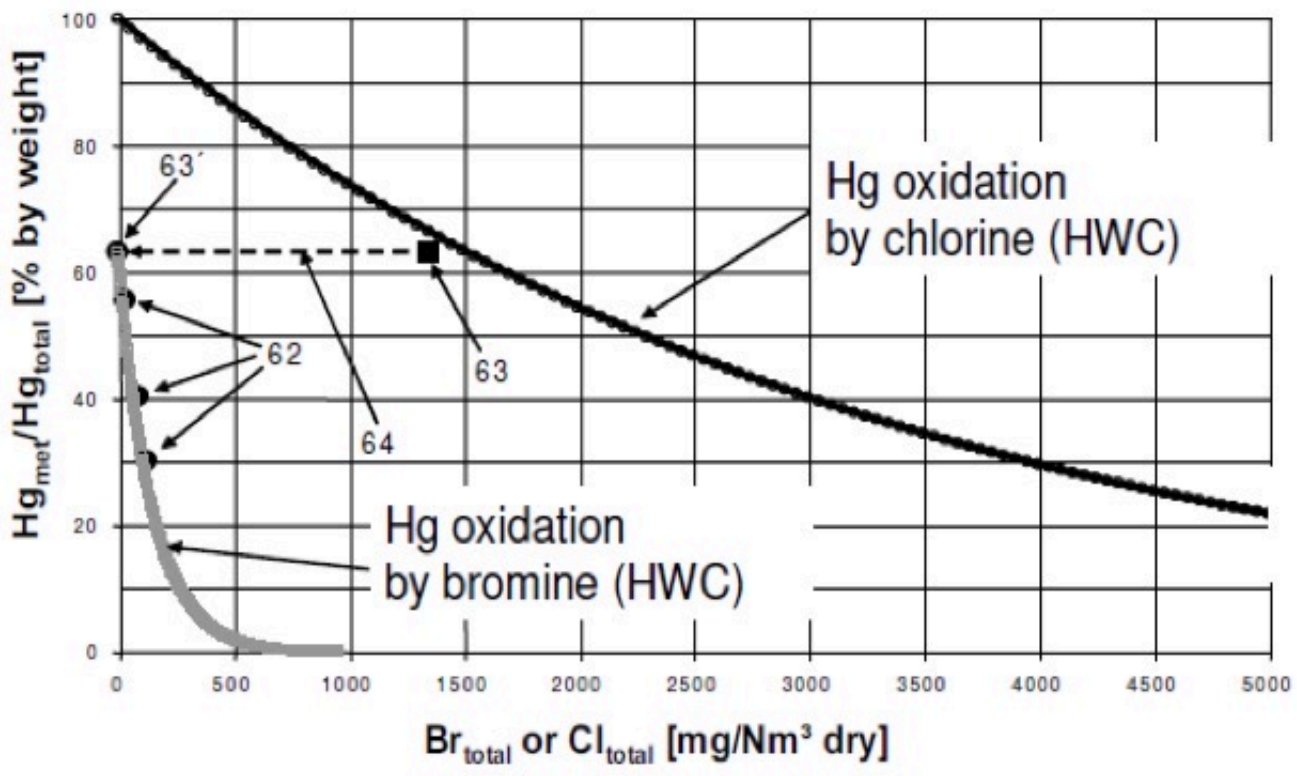
Invention Prof. Vosteen (2000)





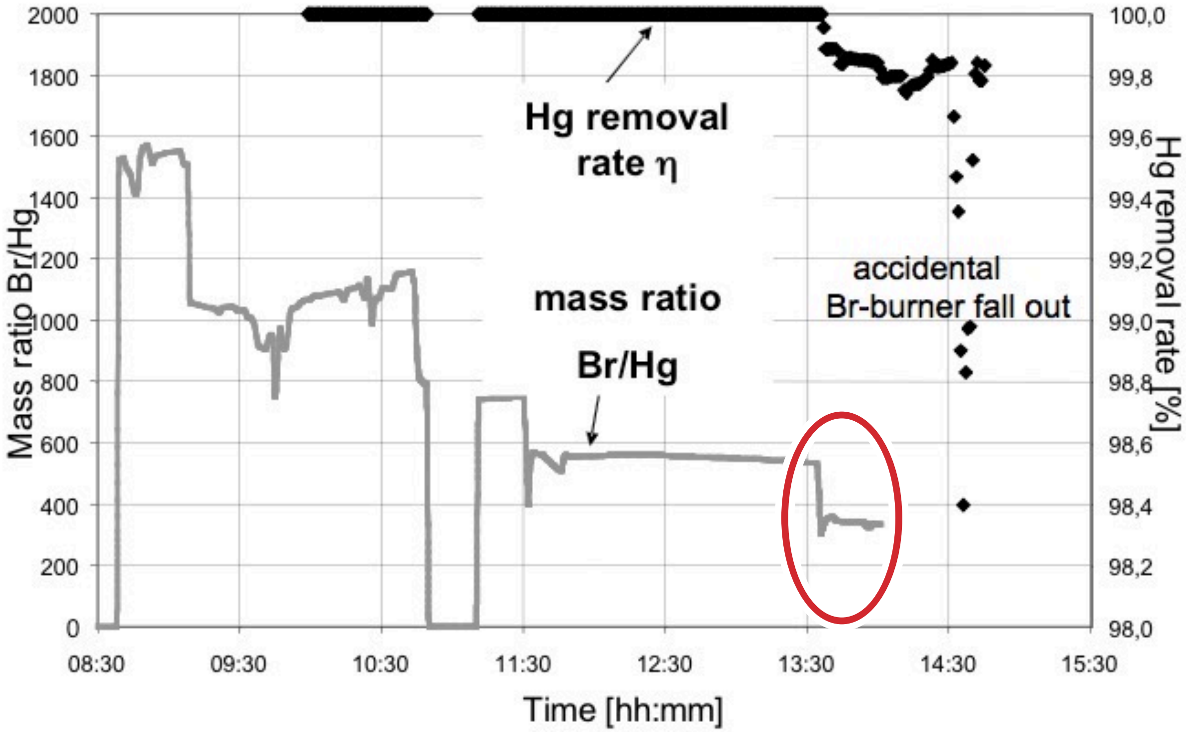
Mercury concentration Hg_{tot} at the stack of the CURRENTA Waste Management Center in Leverkusen-Bürrig

Example: Bromine versus Chlorine



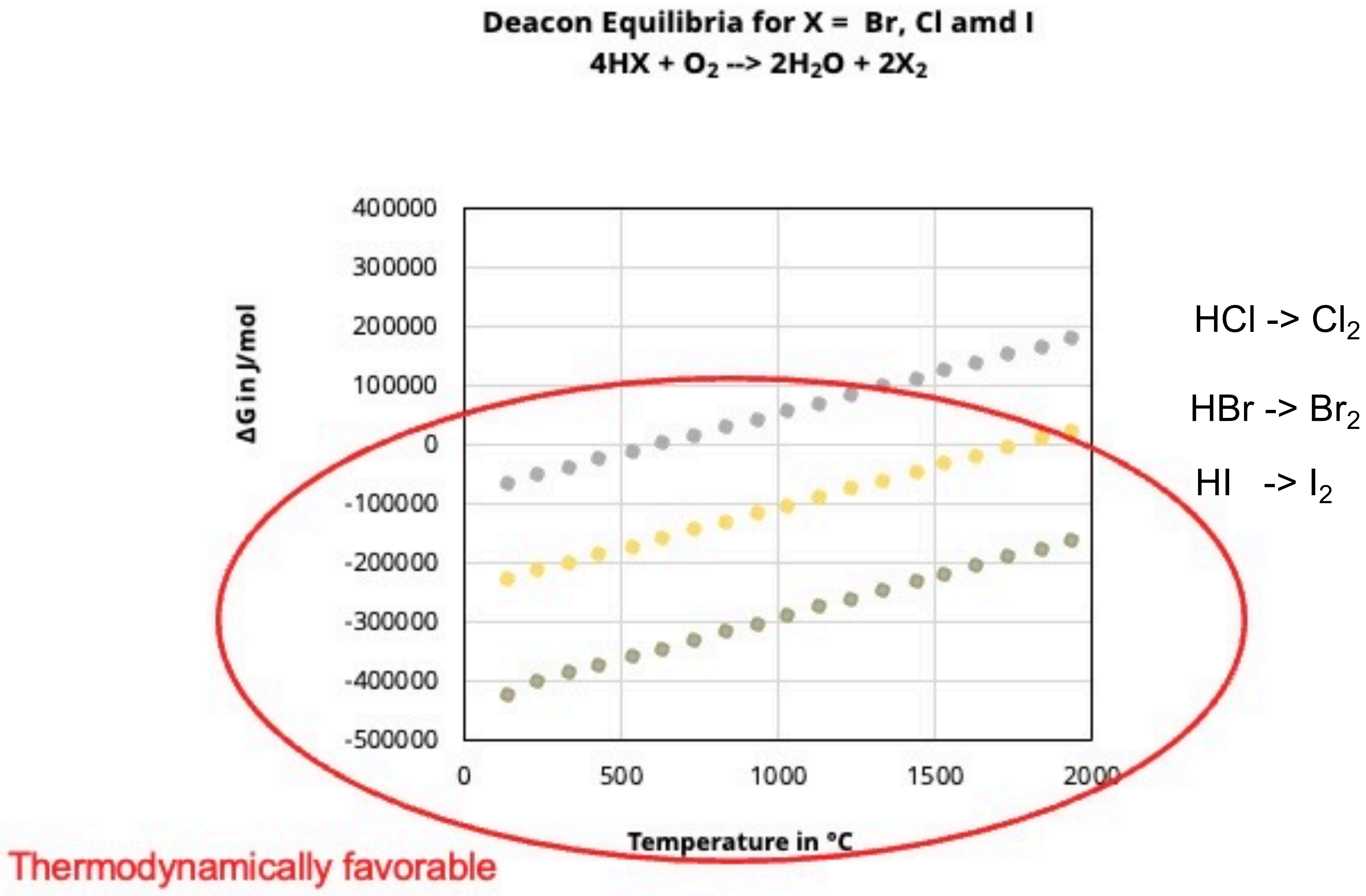
Source: B. W. Vosteen et al., EP 1 386 655 B1

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

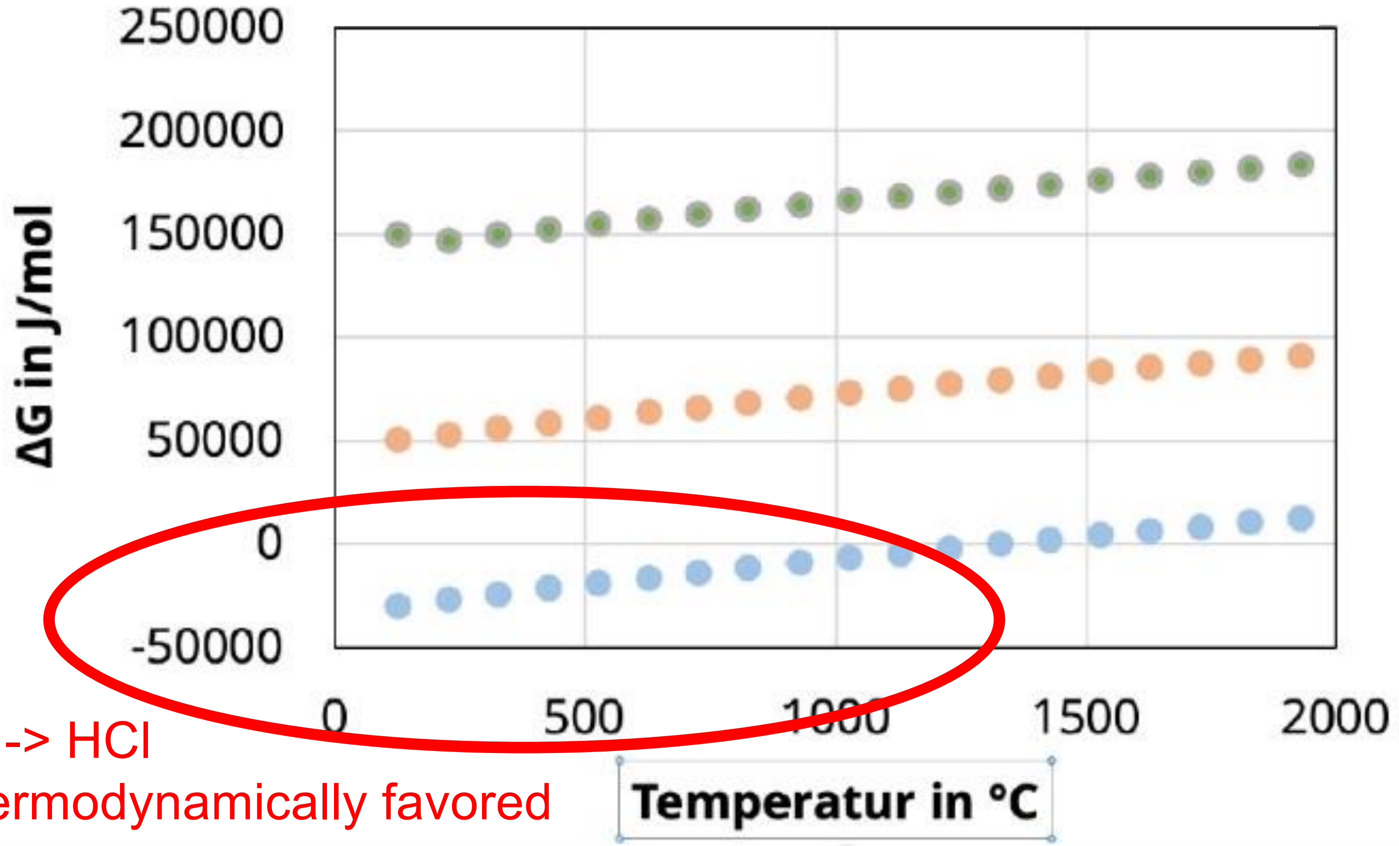


Mass ratio Br/Hg = 100 … 500 needed ("without high dust SCR")

Anne-Christin Knopp
TU Dresden



Griffin Equilibria for X = Br, Cl amd I
$SO_2 + H_2O + X_2 \text{-->} SO_3 + 2HX$



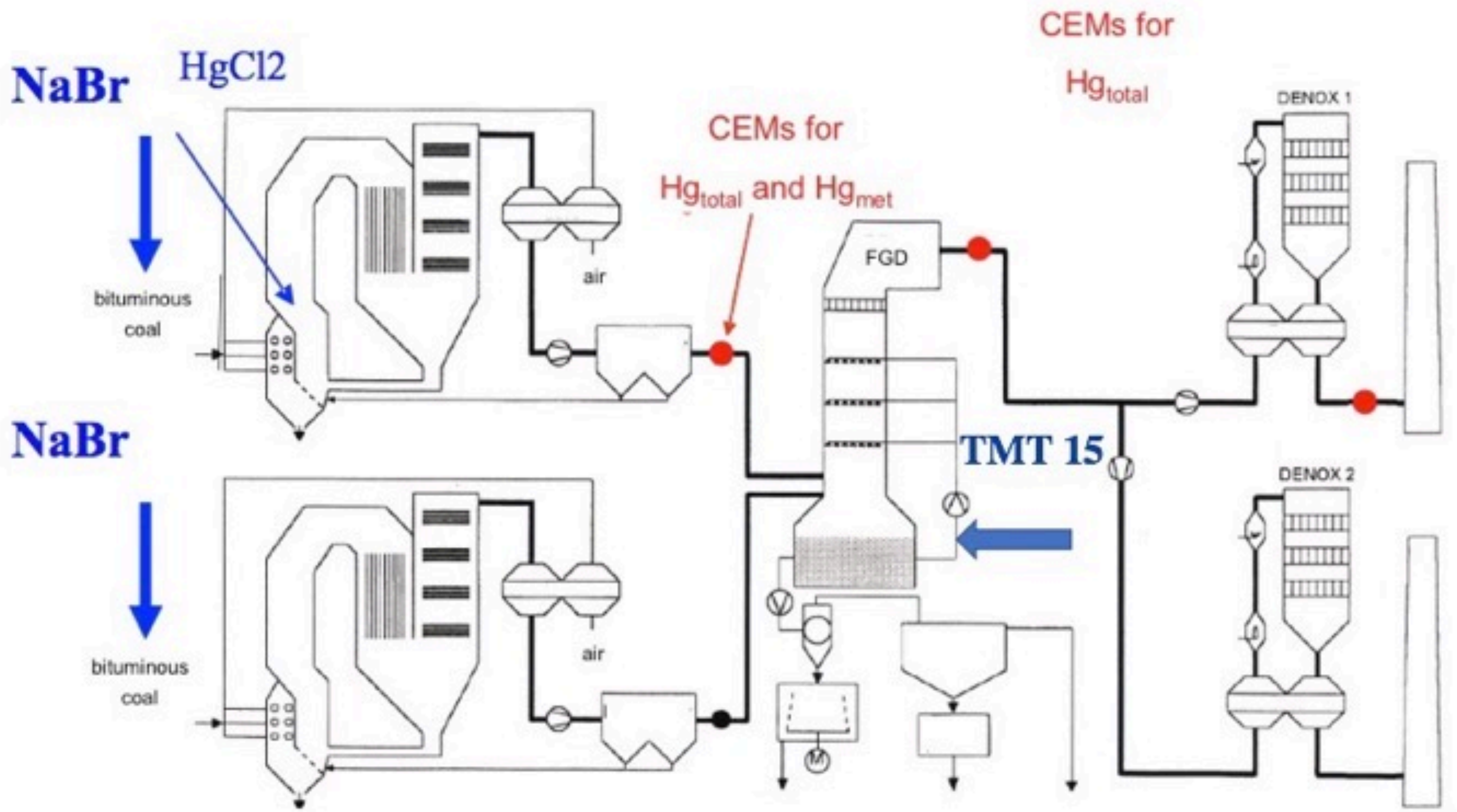
I_2 -> HI

Br_2 -> HBr

Cl_2 -> HCl

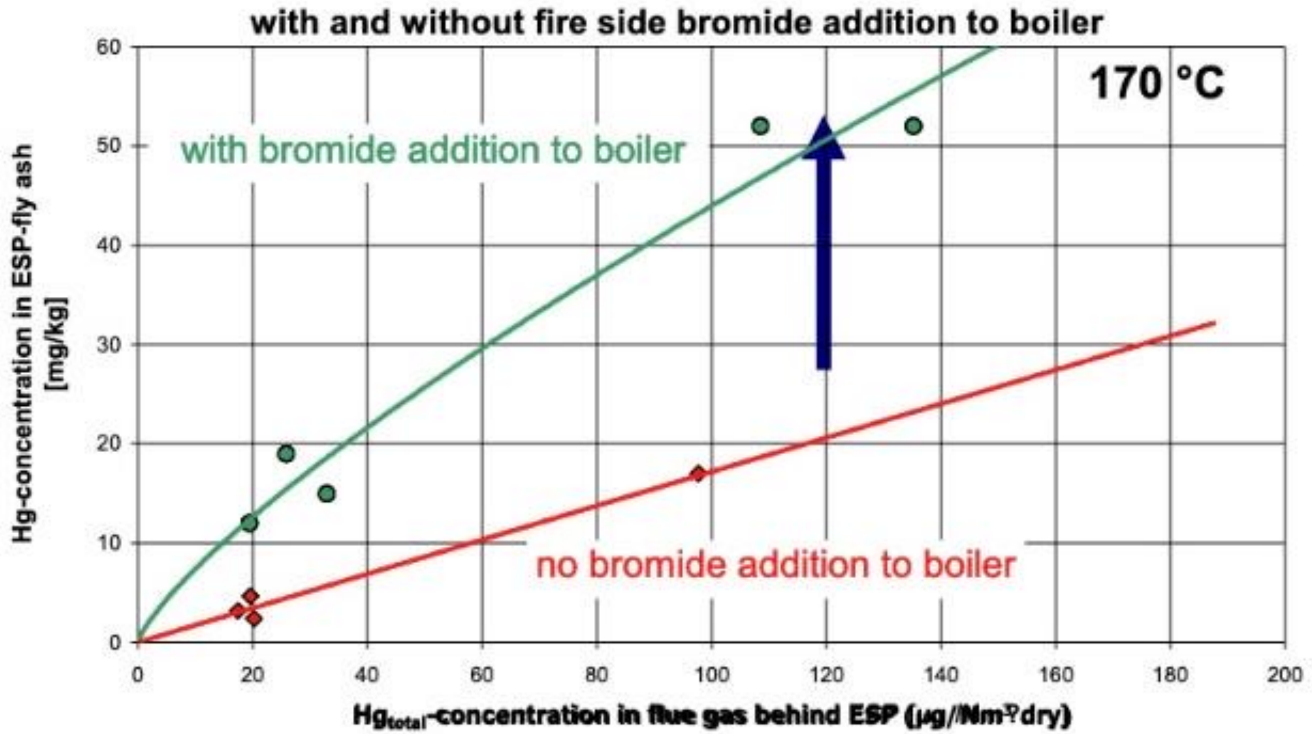
Cl_2 -> HCl
Thermodynamically favored

Industrial Tests at coal-fired utility of BAYER/CURRENTA with NaBr and TMT15 in 2001 (Power Plant N230 in Uerdingen)



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

Sorption isothermes of the ESP-fly ash of high LOI (22,3 % UBC)



Source: Vosteen, Nolte et al.: „Chlorine- and bromine-enhanced Hg sorption on ESP flyash from a coal-fired slag-tap boiler and on cement raw meal“, VDI Seminar 431802, September 29 - 30, 2003 in Duesseldorf (Germany)

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4. Hg Emission Control Activities
   at Bełchatów Unit 5 and Unit 14 in 2017/ 2018
5. Modelling VOSTEEN of these Tests from 2017/2018
6. Recent Long-Time Testings at Bełchatów Unit 3 and Unit 14
7. Bromide Storage Tanks and Dosing Devices
8. Conclusions

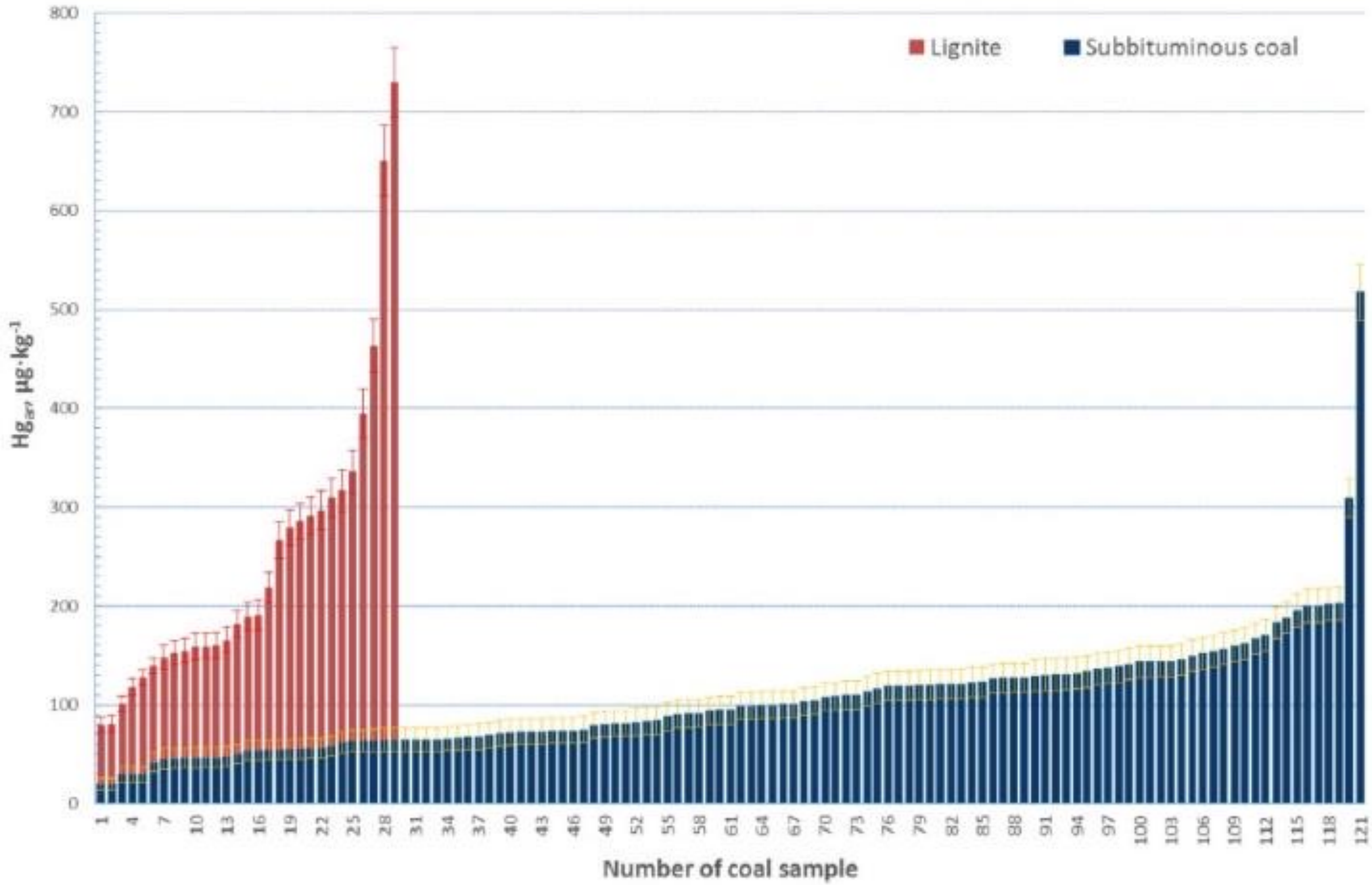

Fig. 3. Mercury content in analyzed samples.

Table 3
Proximate and ultimate analysis of tested coals.

Component	Plant 1	Plant 2	Plant 3
Hg (ppb)	66 ± 9	100 ± 15	596 ± 99
Cl (ppm)	1040 ± 50	750 ± 45	88 ± 12
Br (ppm)	15.0 ± 1.1	14.1 ± 0.6	4.2 ± 0.1
S (wt.%)	0.49 ± 0.01	0.64 ± 0.04	1.18 ± 0.06
Moisture[a] (wt.%)	9.0 ± 0.4	9.8 ± 0.7	52.9 ± 0.6
Ash (wt.%)	26.8 ± 1.6	20.5 ± 2.4	25.3 ± 2.9
$q_{p,net}$[a] (MJ kg^{-1})	22.91 ± 0.65	23.14 ± 0.28	7.42 ± 0.37

[a] Dry basis or as-received.

corresponds to Bełchatów Lignite as fired

Mercury Balance performed at Bełchatów Unit 4 in 2016

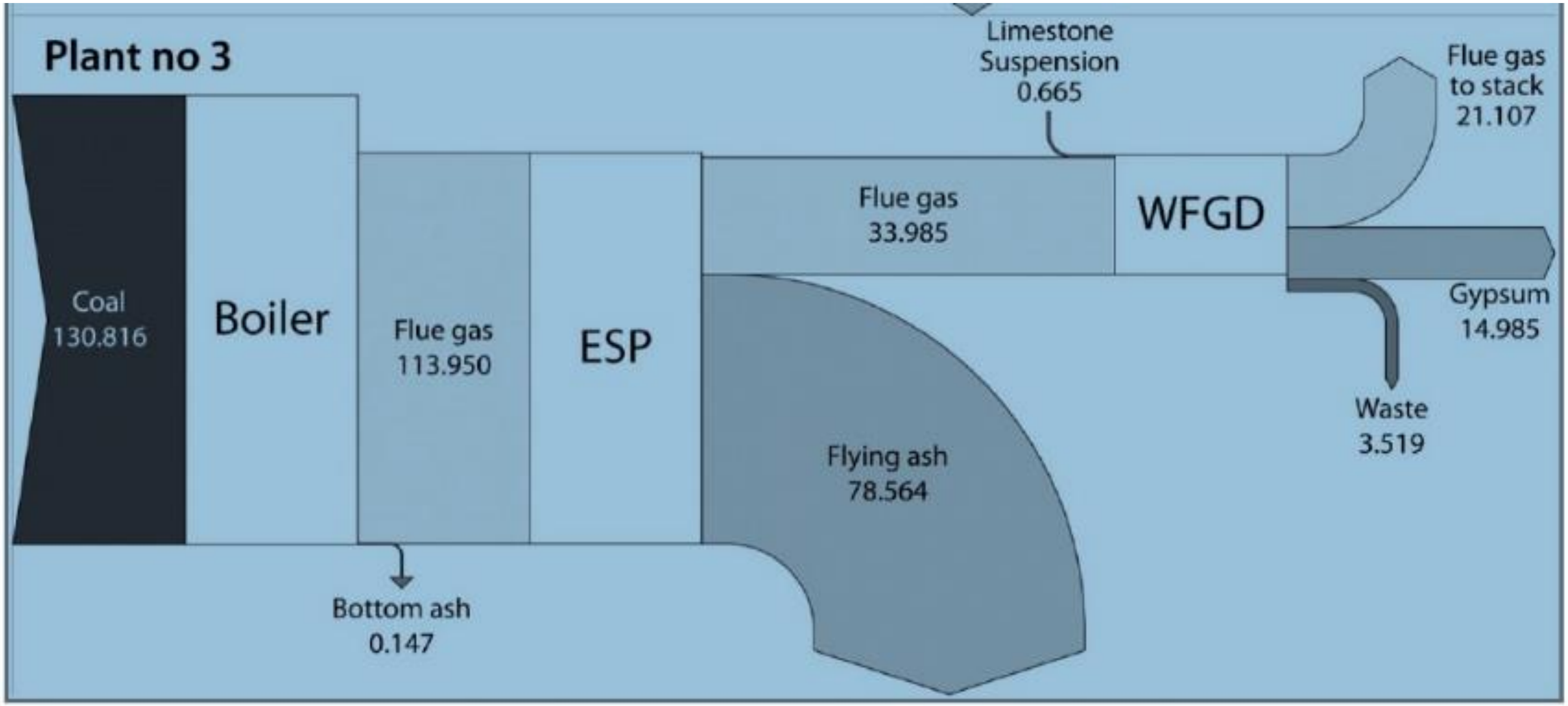

Fig. 7. Sankey diagrams of mercury distribution (mercury stream, $g \cdot h^{-1}$).

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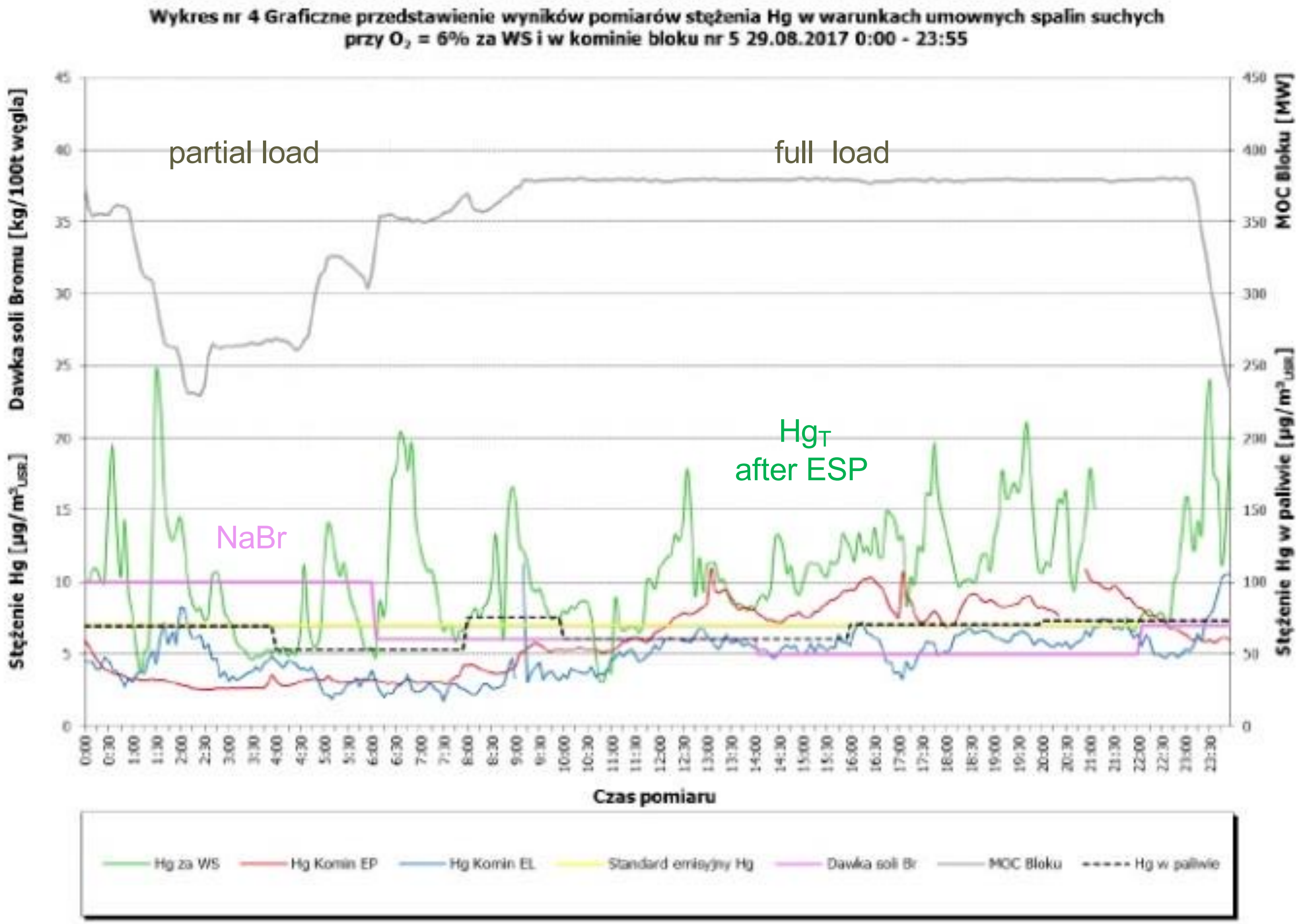
Promissing test results at Unit 5 in August 29th, 2017



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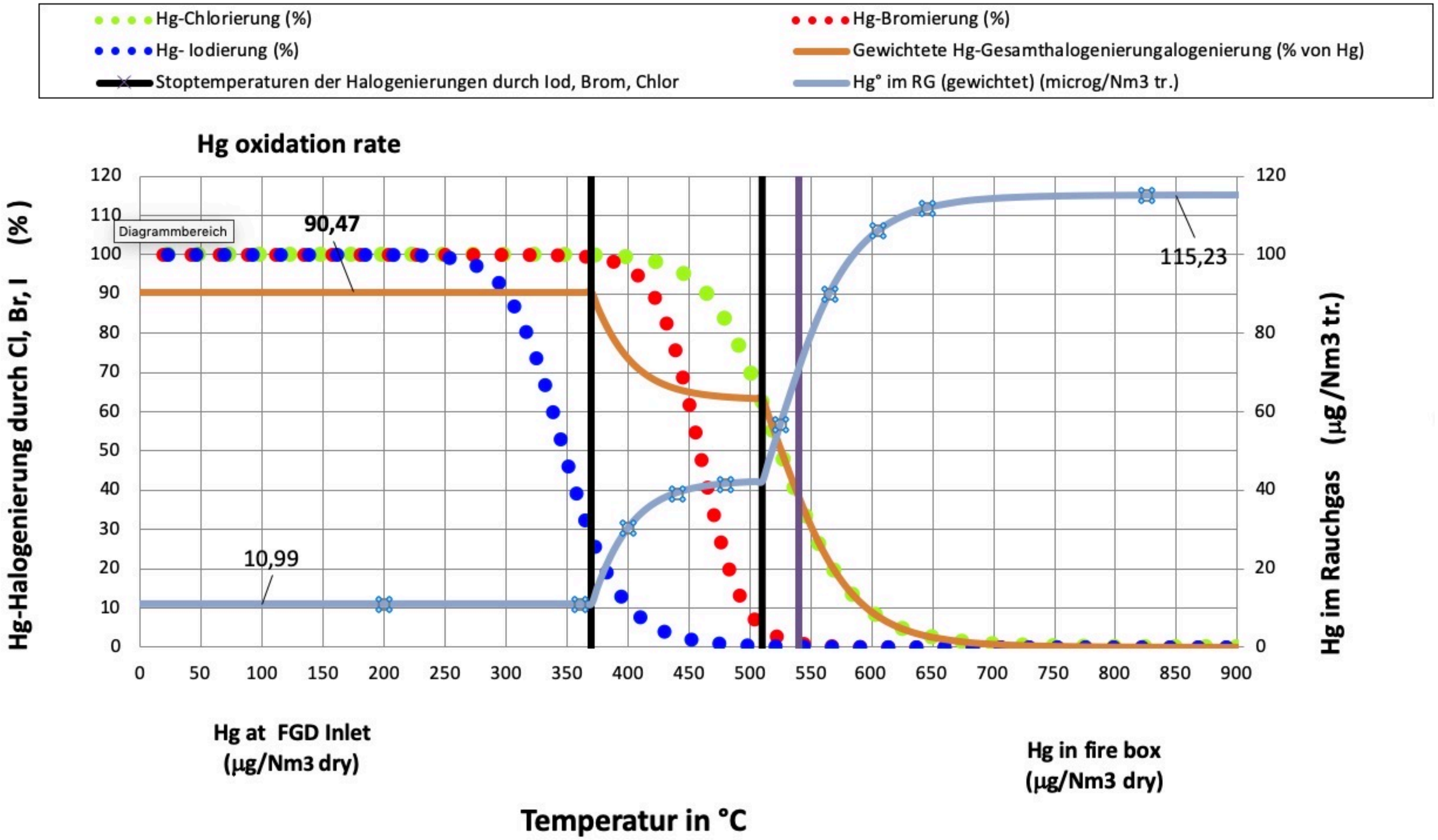
Modelling of the mercury oxidation by halogens (Stoptemperature method of Prof. Vosteen)

Example for a calculation point with given Cl (native) , Br (not added) and I (added)



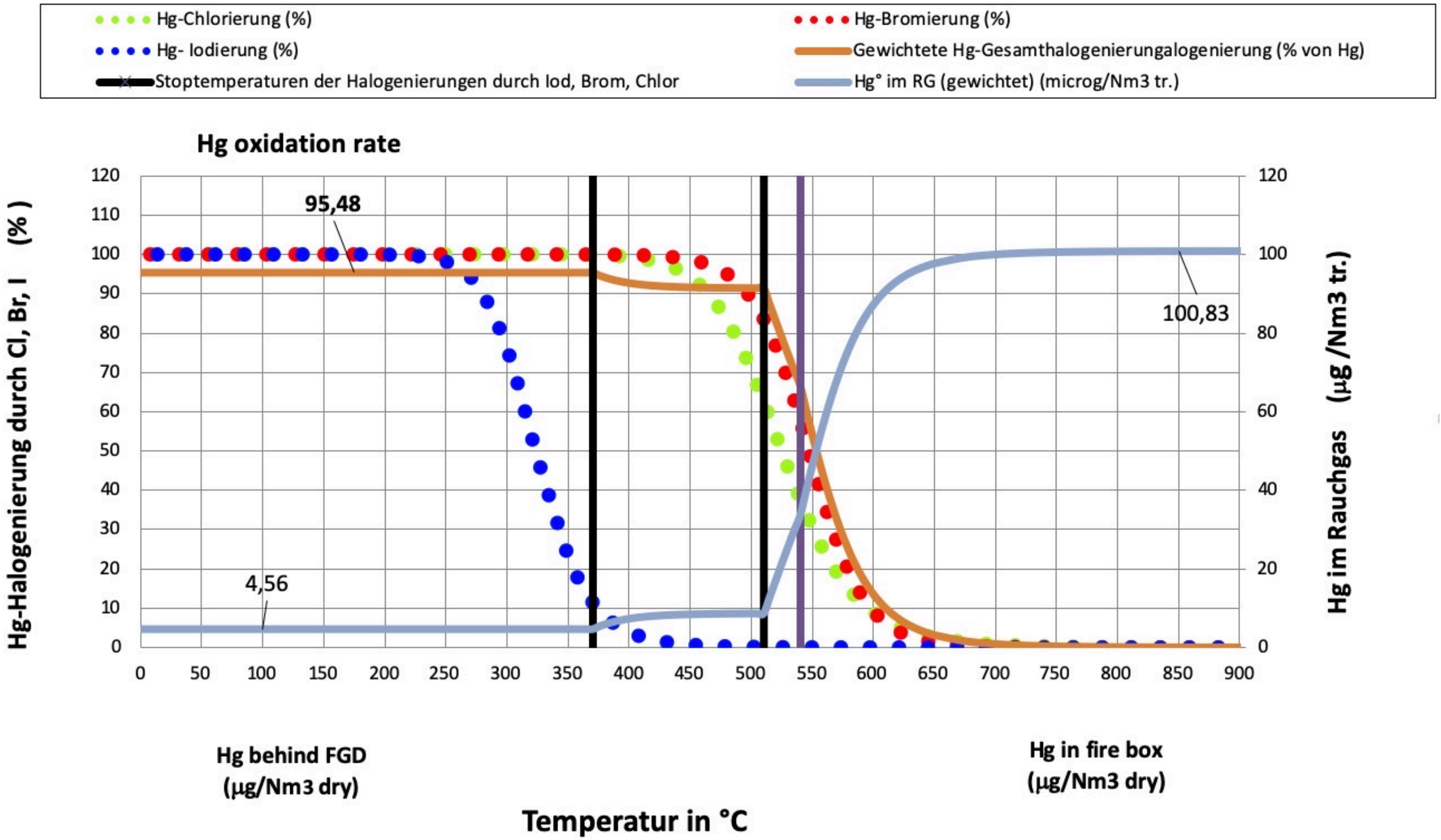
Analyzing the Test Results from 2017/2018 with help of the Vosteen's modelling programm delivered the following Stoptemperatures:

Stopptemperatur der Hg-Chlorierung(°C)	510
Stopptemperatur der Hg-Bromierung (°C)	540
Stopptemperatur der Hg-Iodierung (°C)	370

Fig. 14: Defined Stop-Temperatures chosen for Unit 3*)

*) Please note: The model was written in German language (engl. Stop-Temperature is Stopptemperatur in German).

Example for a calculation point with given Cl (native) , Br (added) and I (added)



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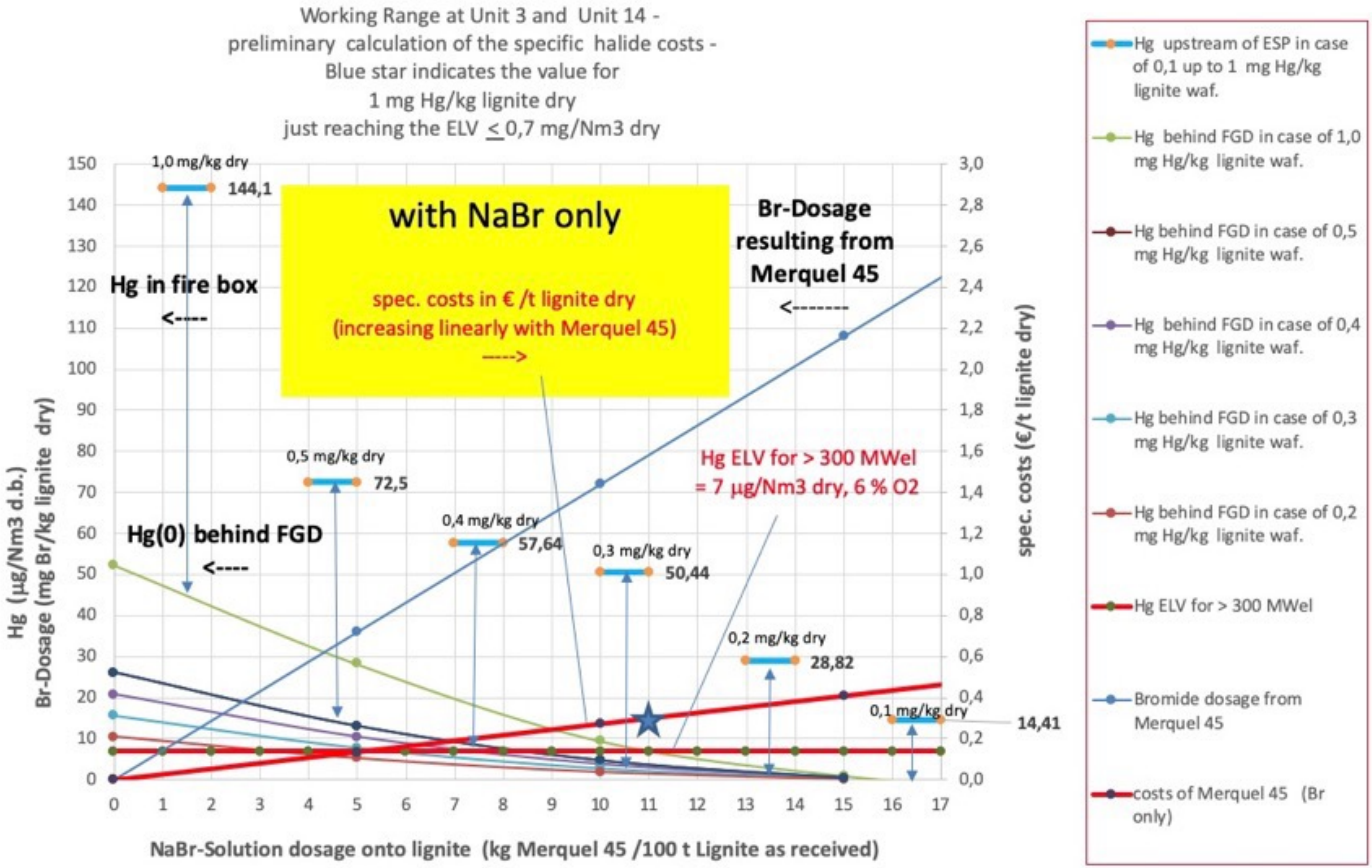
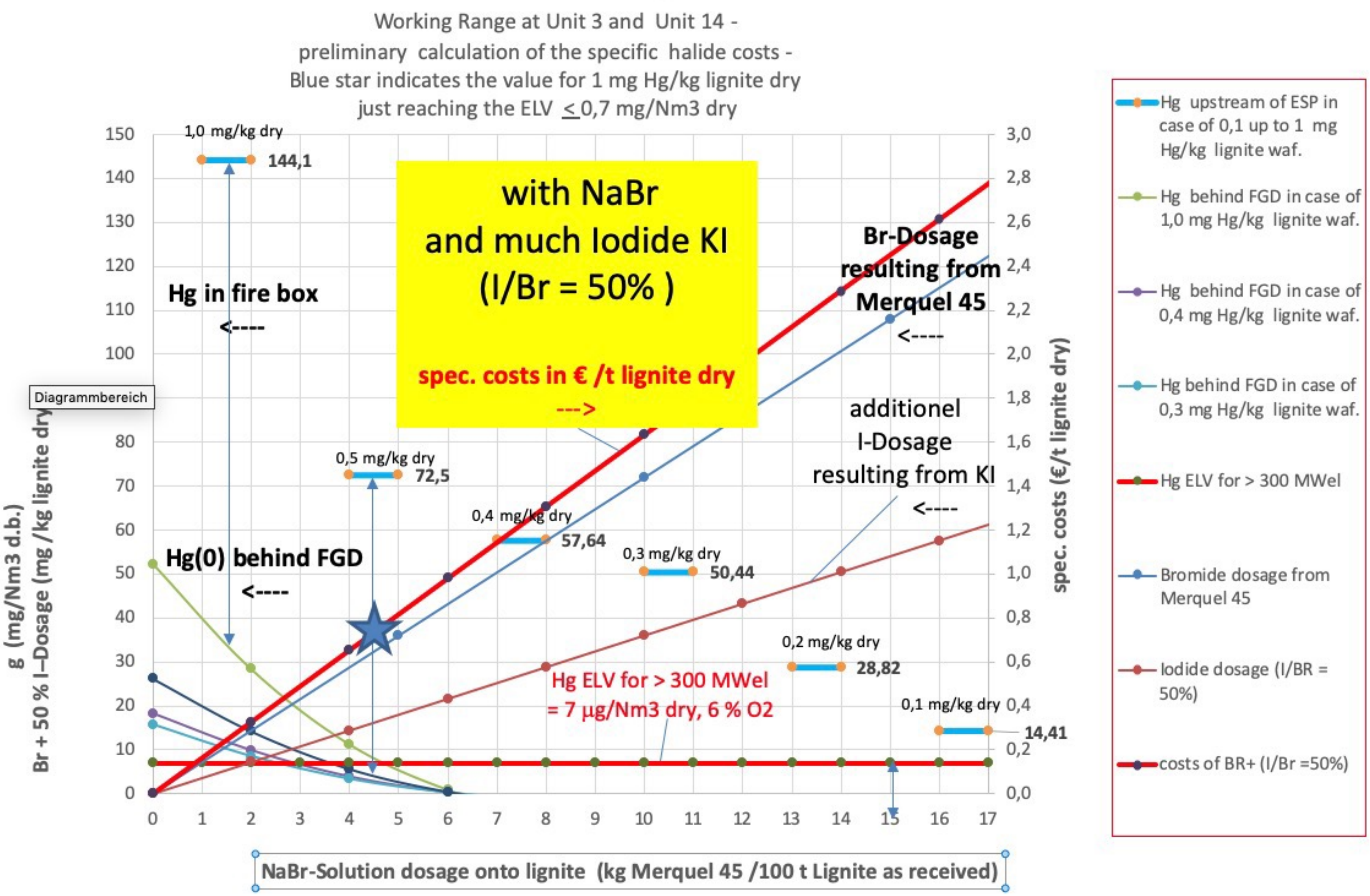
VOSTEEN Consulting



PGE Górnictwo i Energetyka Konwencjonalna S.A.

VOSTEEN Consulting



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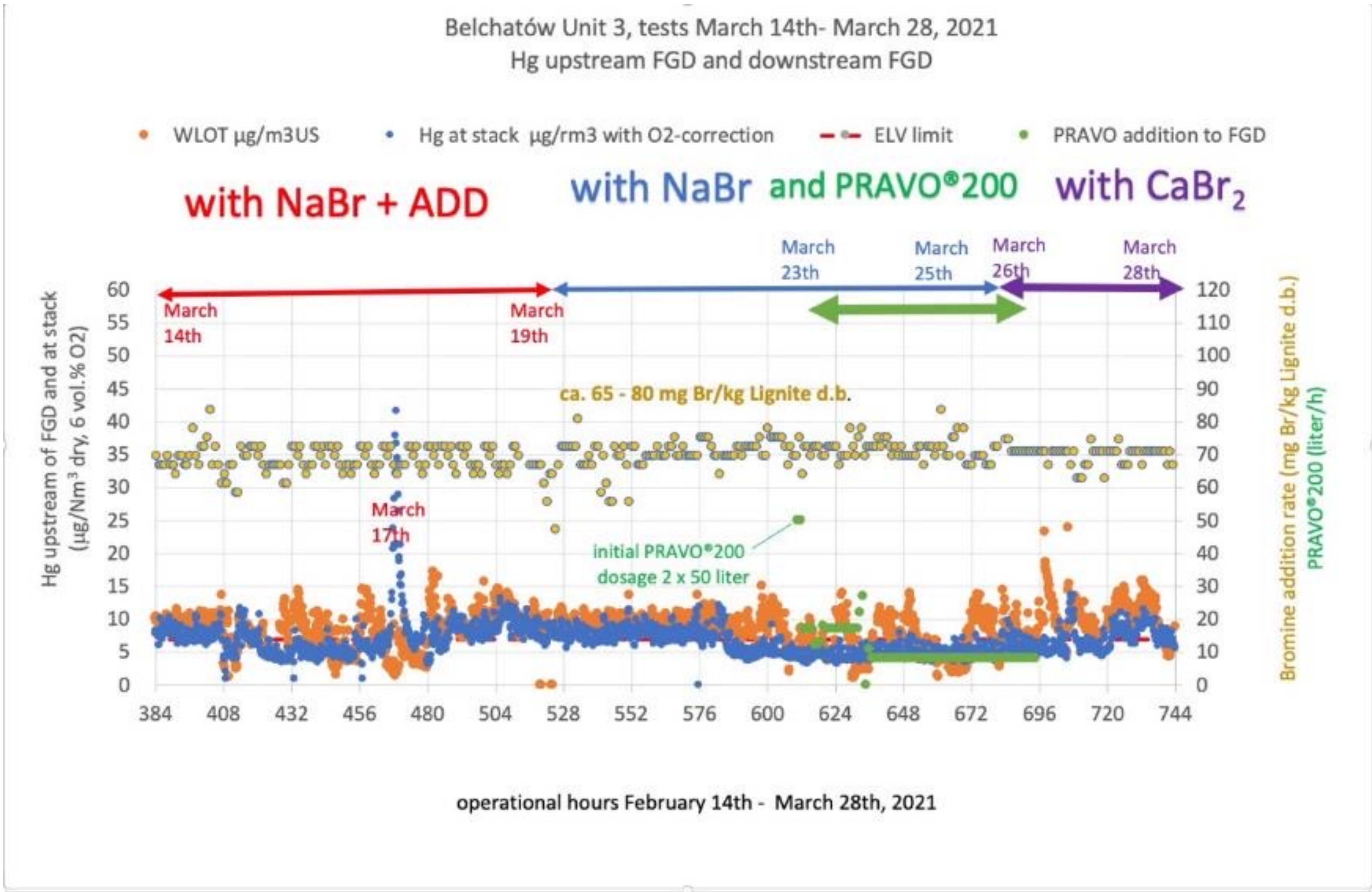
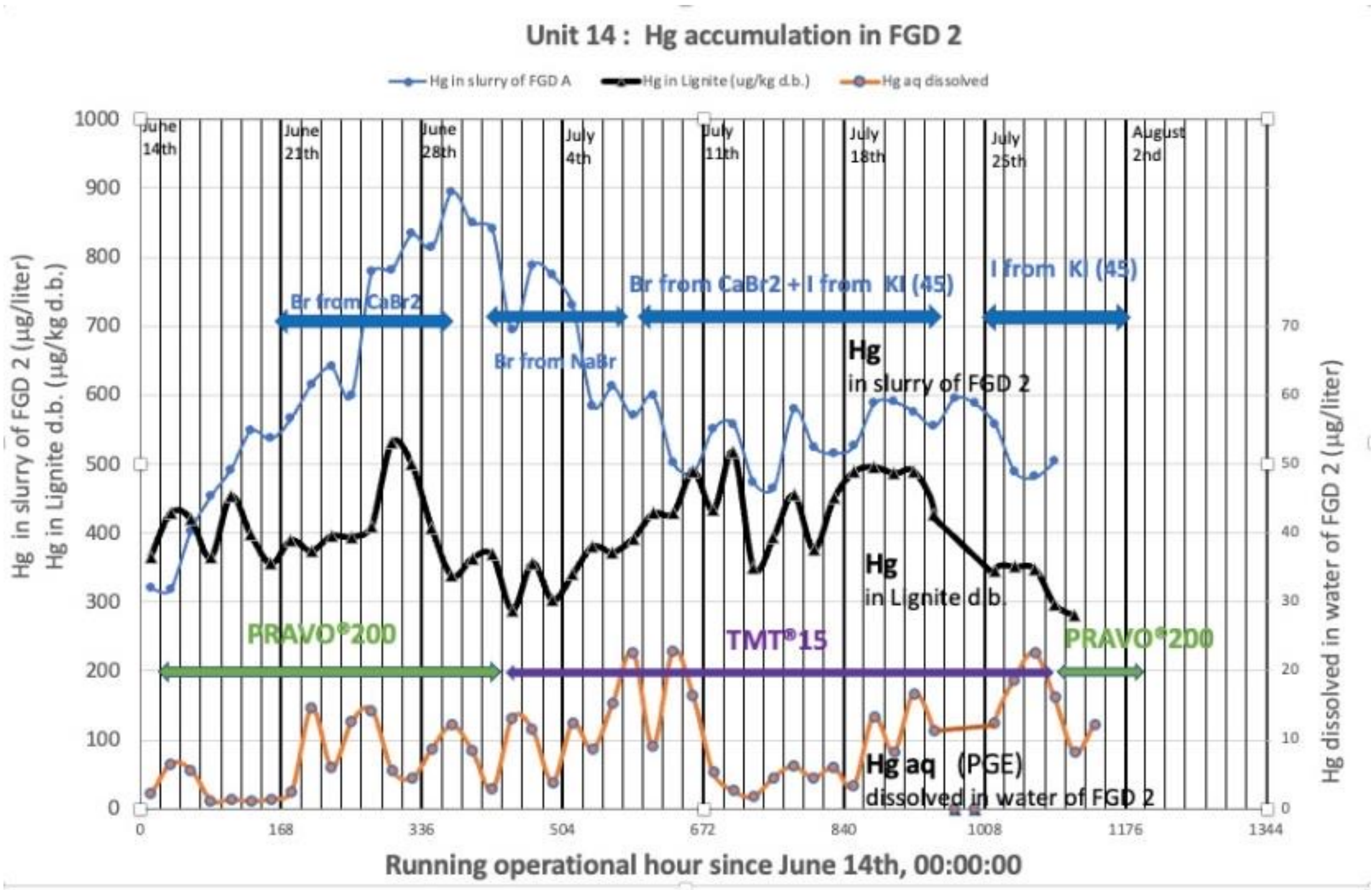
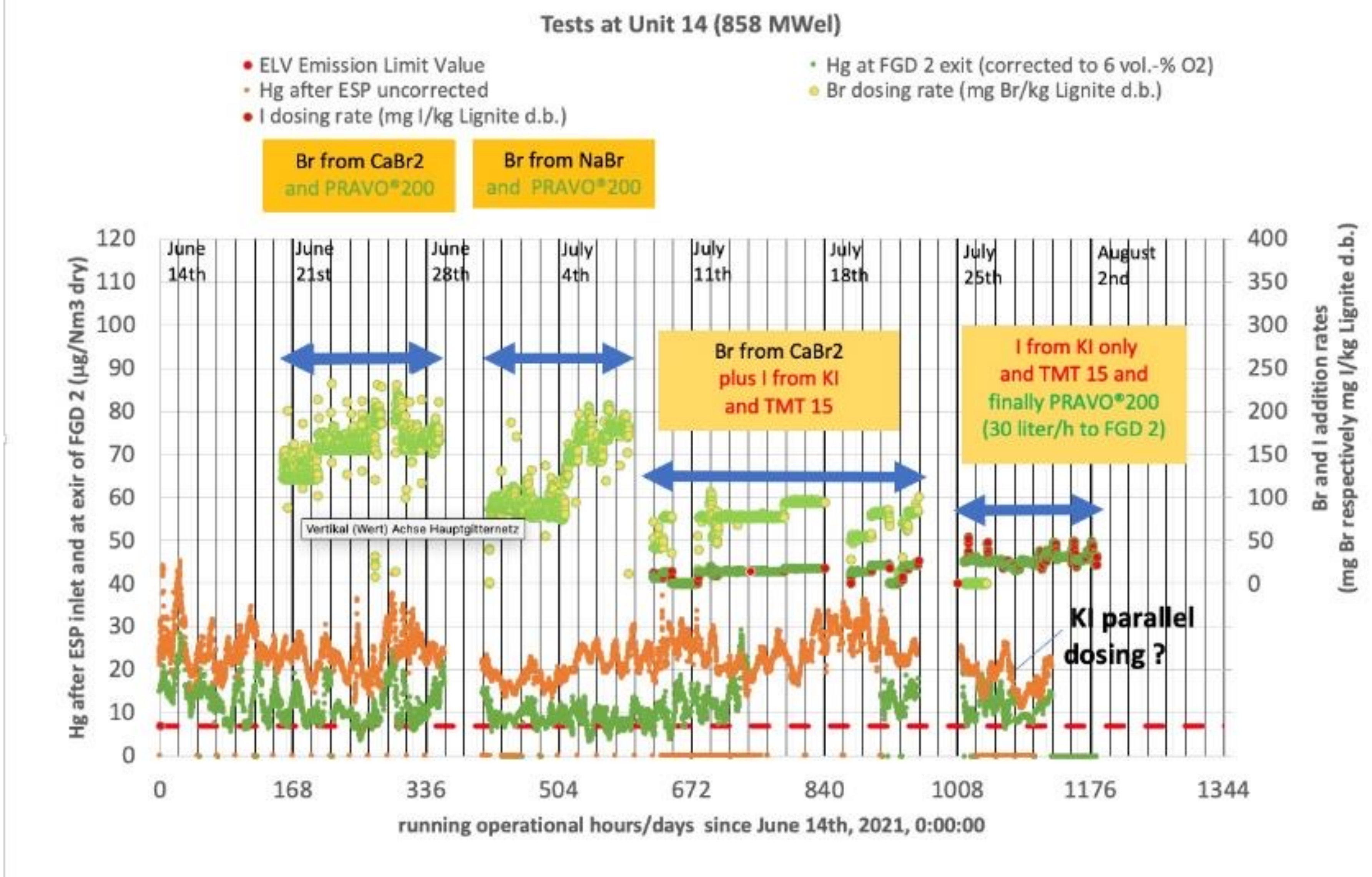
Long-Time Testings at Bełchatów Unit 3 in 2021

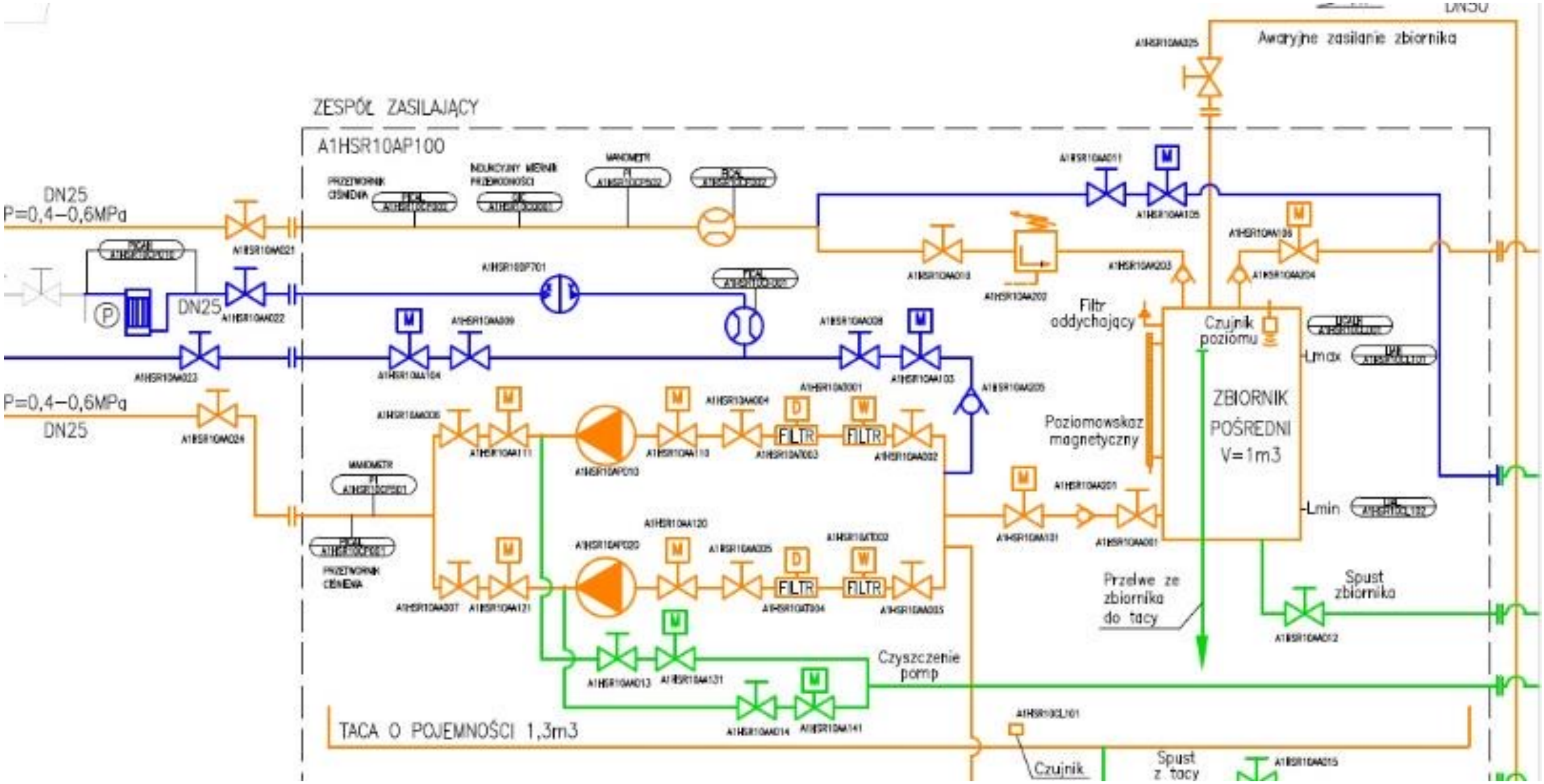

Belchatów Unit 3, tests March 14th- March 28, 2021
Hg upstream FGD and downstream FGD
WLOT µg/m3US
Hg at stack µg/rm3 with O2-correction
ELV limit
PRAVO addition to FGD
with NaBr + ADD
with NaBr and PRAVO®200
with CaBr2
March 14th
March 19th
March 23th
March 25th
March 26th
March 28th
March 17th
ca. 65 - 80 mg Br/kg Lignite d.b.
initial PRAVO®200 dosage 2 x 50 liter
Hg upstream of FGD and at stack (µg/Nm³ dry, 6 vol.% O2)
Bromine addition rate (mg Br/kg Lignite d.b.)
PRAVO®200 (liter/h)
operational hours February 14th - March 28th, 2021

Long-Time Testings at Bełchatów Unit 14 in 2021

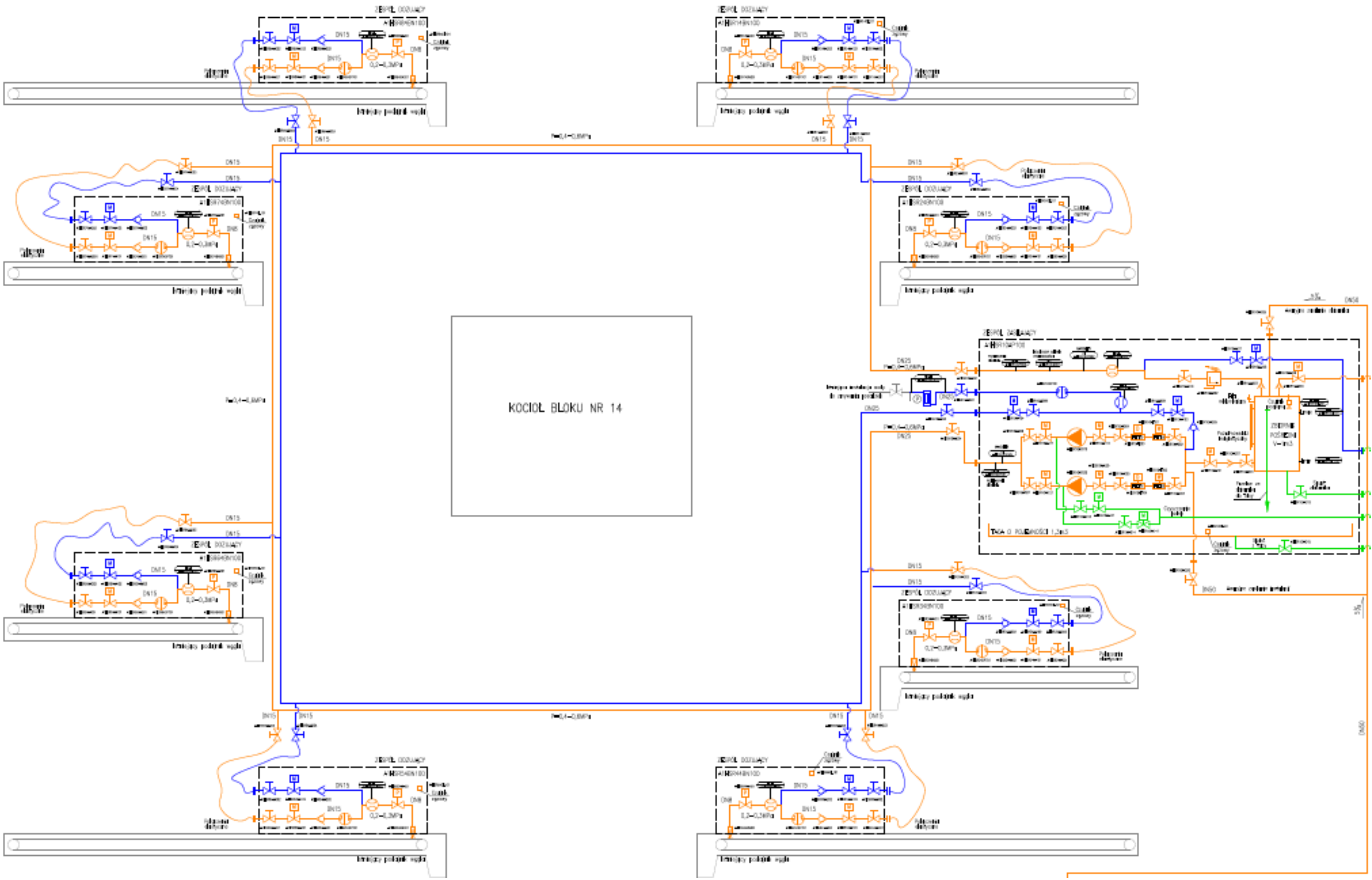

Unit 14 : Hg accumulation in FGD 2
Hg in slurry of FGD A
Hg in Lignite (ug/kg d.b.)
Hg aq dissolved
Hg in slurry of FGD 2 (µg/liter)
Hg in Lignite d.b. (µg/kg d.b.)
Hg dissolved in water of FGD 2 (µg/liter)
June 14th
June 21th
June 28th
July 4th
July 11th
July 18th
July 25th
August 2nd
Br from CaBr2
Br from NaBr
Br from CaBr2 + I from KI (45)
I from KI (45)
Hg
in slurry of FGD 2
Hg
in Lignite d.b.
PRAVO®200
TMT®15
PRAVO®200
Hg aq (PGE)
dissolved in water of FGD 2
0
100
200
300
400
500
600
700
800
900
1000
0
10
20
30
40
50
60
70
0
168
336
504
672
840
1008
1176
1344
Running operational hour since June 14th, 00:00:00


Tests at Unit 14 (858 MWel)
ELV Emission Limit Value
Hg after ESP uncorrected
I dosing rate (mg I/kg Lignite d.b.)
Hg at FGD 2 exit (corrected to 6 vol.-% O2)
Br dosing rate (mg Br/kg Lignite d.b.)
Br from CaBr2 and PRAVO®200
Br from NaBr and PRAVO®200
Br from CaBr2 plus I from KI and TMT 15
I from KI only and TMT 15 and finally PRAVO®200 (30 liter/h to FGD 2)
KI parallel dosing ?
Vertikal (Wert) Achse Hauptgitternetz
June 14th
June 21st
June 28th
July 4th
July 11th
July 18th
July 25th
August 2nd
Hg after ESP inlet and at exir of FGD 2 (µg/Nm3 dry)
Br and I addition rates (mg Br respectively mg I/kg Lignite d.b.)
running operational hours/days since June 14th, 2021, 0:00:00
0
168
336
504
672
840
1008
1176
1344

Agenda



Design of the Bromide Solution Feeding System



Overview of the Bromide Solution Feeding System

Storage tanks

2 x 60 m^3

serving the Units 2-12

Agenda

Conclusion

Emission levels <7 μg/Nm^3 d.b. at stack can be achieved with limited dosing rates of NaBr or $CaBr_2$ solutions, as well.

NaBr is getting more and more expensive. Therefor $CaBr_2$ is recommended.

Iodides are far more effective in mercury oxidation than bromides, Iodide salts or solutions might therefor be used, as well - e.g. in form of KI or NaI-solutions But such iodides have got extremely expensive. Not to be recommended.

Precipitation agents as anorganic PRAVO®200 or organic TMT®15 can both be used as FGD additive to suppress Hg-reemissions and to stabilize the dissolved mercury as solid mercury sulfide or mercury-TMT-complex.

During full load, the oxigen content should not be lowered too much. Otherwise the mercury oxidation will become insufficiient (Deacon reaction needs oxigen).