Optimization of mercury mitigation in pilot plants

VGB Workshop Mercury Control 2016
Berlin, 15./16.June 2016

Dr. Johannes Mayer, Gabriele Böhm
Uniper Technologies GmbH

Investigation of Mercury Mitigation

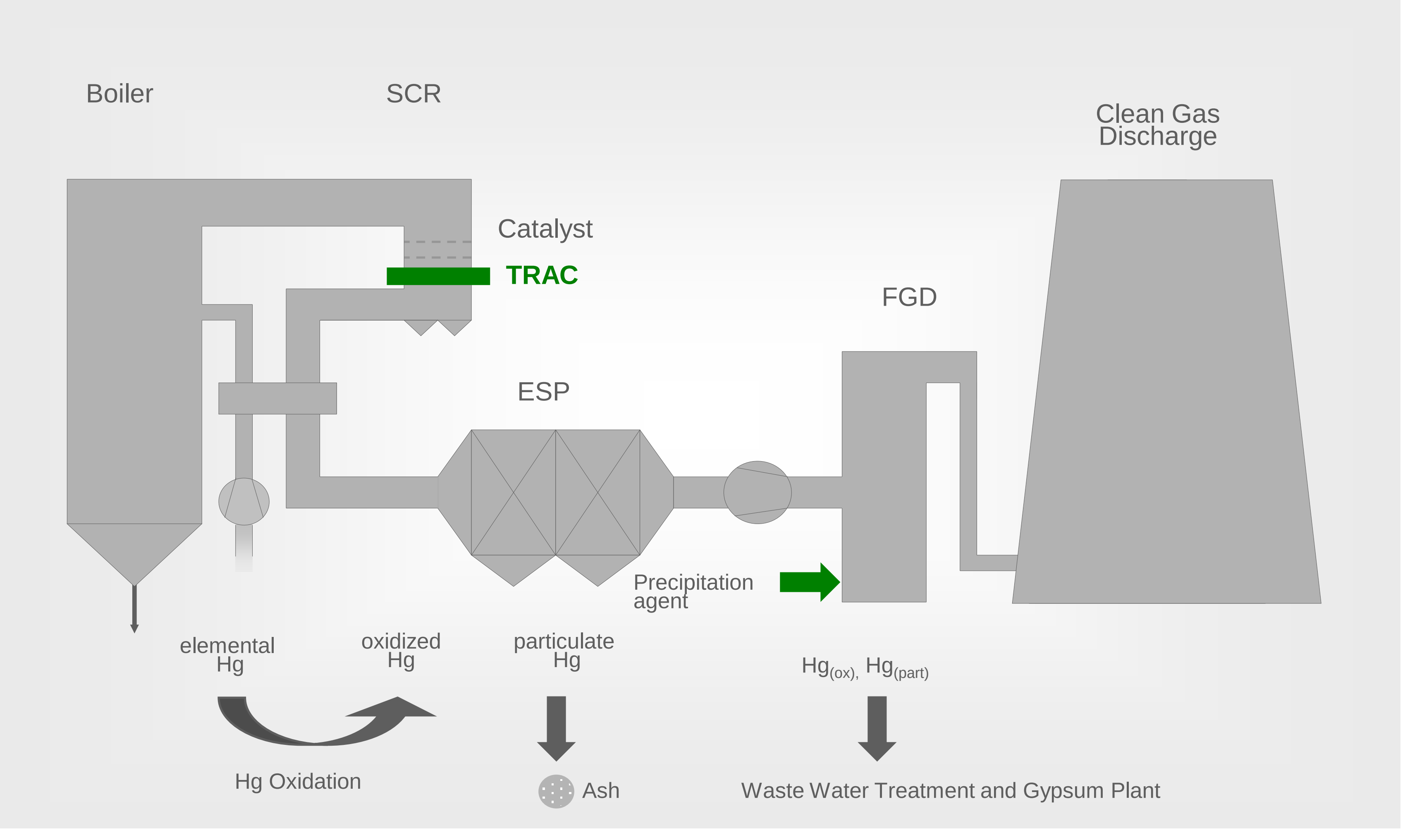
30 years of experience in the behaviour of mercury and other trace elements

Development of own measuring and sampling methods and specific analytical procedures

Development and operation of lab-scale test and pilot plants (SCR, FGD, FGD-WWT)

Various tests at lab-scale and full-scale plants for mitigation of mercury releases to air and water

Reduction of Mercury Release to Air



TRAC: TRiple **A**ction **C**atalyst

J. Mayer, G. Böhm – Uniper Technologies GmbH – VGB Workshop *Mercury Control 2016*, Berlin, 16. June 2016

1. Improvement of Mercury Oxidation

Use of a TRAC catalyst

- Use of a specific mercury oxidizing SCR catalyst (TRAC) by E.ON (today Uniper) for the first time in Europe. Start of operation in 2010 in Unit 5 of Staudinger power plant (near Frankfurt)

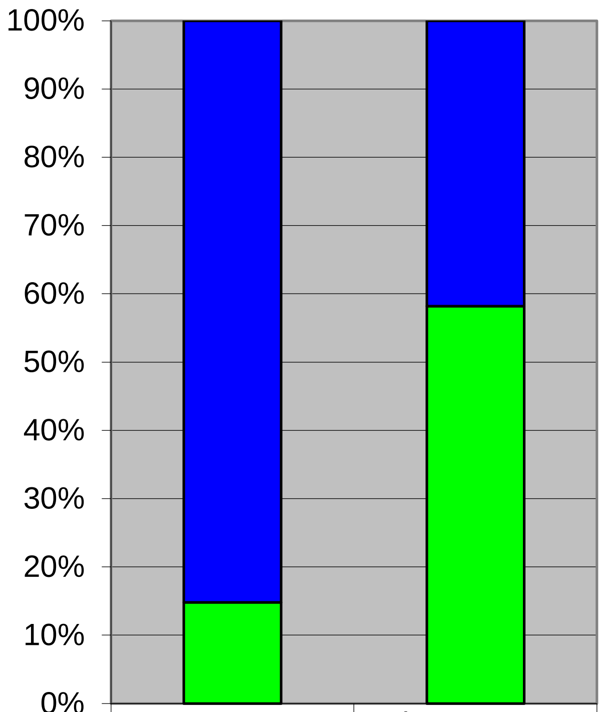
- This technique was developed by Babcock - Hitachi in Japan initially for the US market.

- Designed for the simultaneous reduction of NOx and oxidation of mercury in combination with a low SO_2 conversion rate (SO_2 oxidation to SO_3)

1. Improvement of Mercury Oxidation

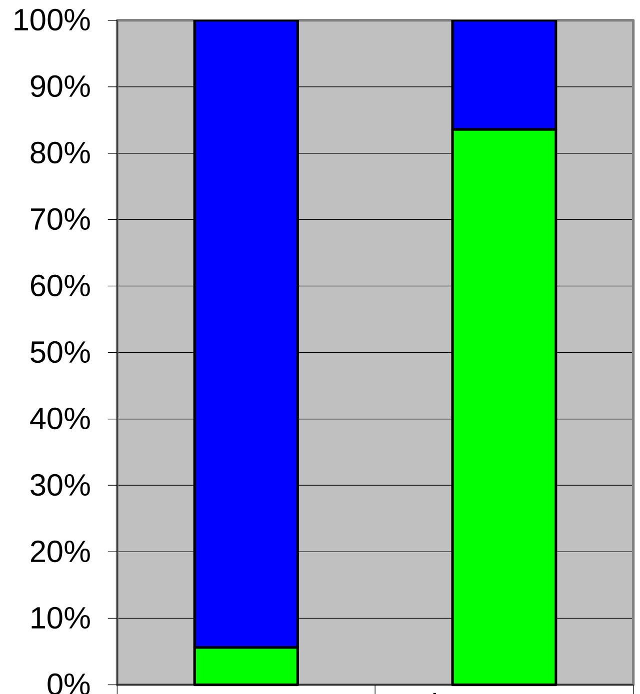
Mercury oxidation across the SCR plant

before Installation of TRAC



	upstream SCR	downstream SCR
Hg (0) in %	85,2	41,8
Hg (ox) in %	14,8	58,2

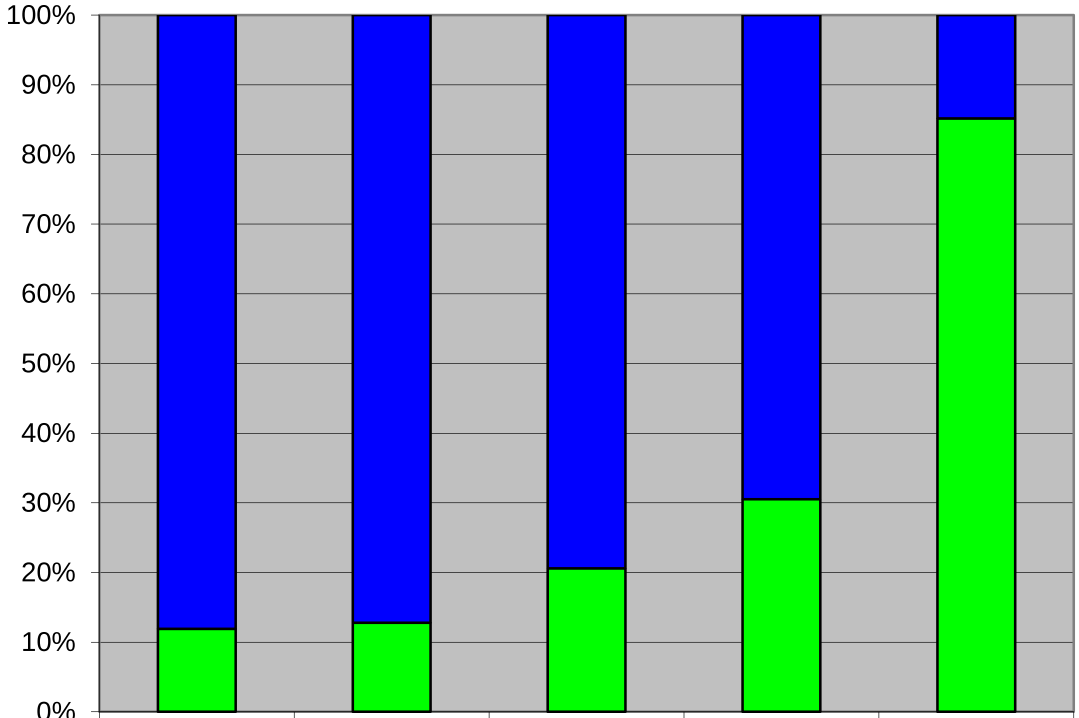
after installation of TRAC



	upstream SCR	downstream SCR
Hg (0) in %	94,4	16,4
Hg (ox) in %	5,6	83,6

1. Improvement of Mercury Oxidation

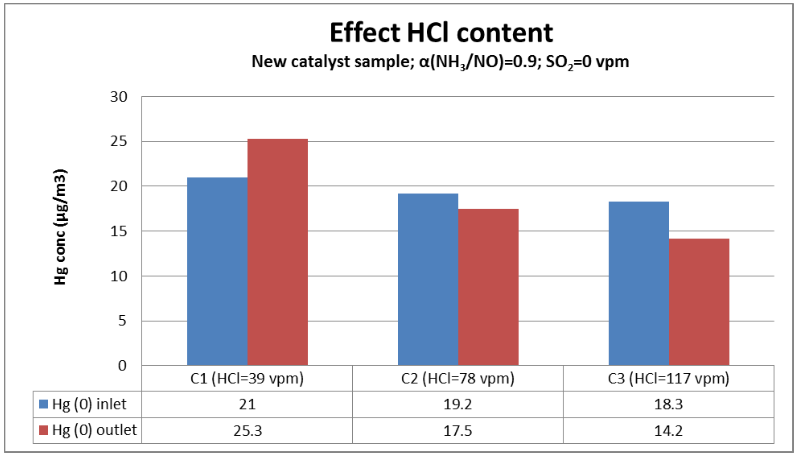
Mercury oxidation of individual catalyst layers



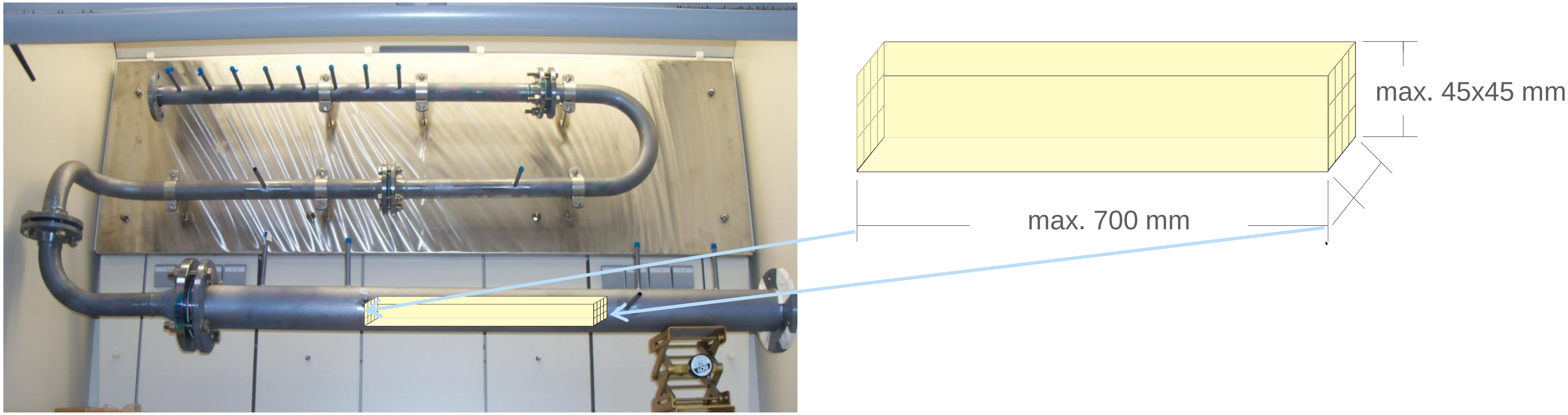
	upstream SCR	downstream 1. layer	downstream 2. layer	downstream 3. layer	downstream SCR
Hg (0) in %	88,1	87,2	79,4	69,5	14,8
Hg (ox) in %	11,9	12,8	20,6	30,5	85,2

1. Improvement of Mercury Oxidation

Semi-bench scale SCR reactor



- Operation of a semi-bench scale reactor for measurement of mercury oxidation since 2013
- Comparison of different catalysts under power plant conditions
- Investigation of the impact of temperature and flue gas composition (Cl, SO_2, NH_3,...) on mercury oxidation activity
- Simulation of different plant loads
- Simulation of the installation position (layer)



2. Avoidance of Mercury Re-Emission

Use of the UTG lab-scale FGD

- The UTG lab-scale FGD is used for investigation of reasons for, and mitigation of, mercury re-emissions.
- The continuously operating lab-scale plant offers the opportunity to simulate operation by use of actual FGD suspension from individual plant but without the risk of emission limit exceedance at the full-scale plant.
- One or more individual parameters can be specifically changed to investigate their influence on the emissions of SO_2 and mercury.

2. Avoidance of Mercury Re-Emission

Requirements for a lab-scale FGD

1 : 1.000.000

Flue gas volume flow: 1 m³/h

Temperature range: 40–65 °C

Sump volume: 1 l

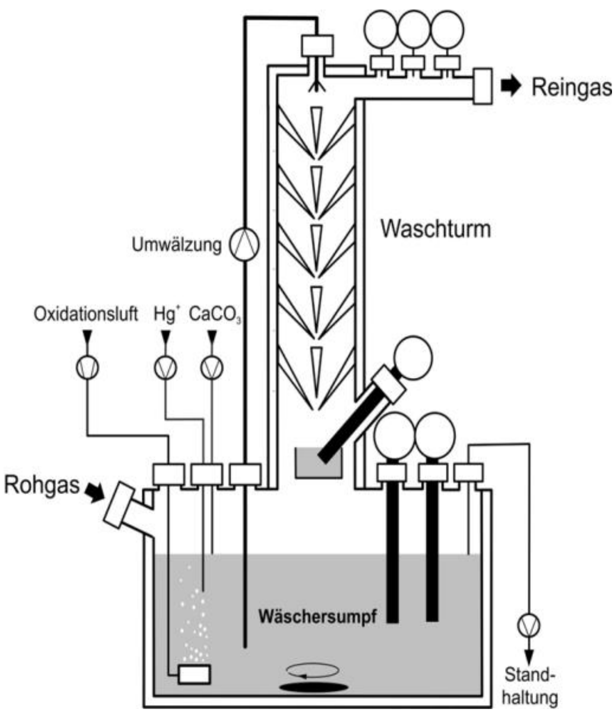
L/G: 10–50

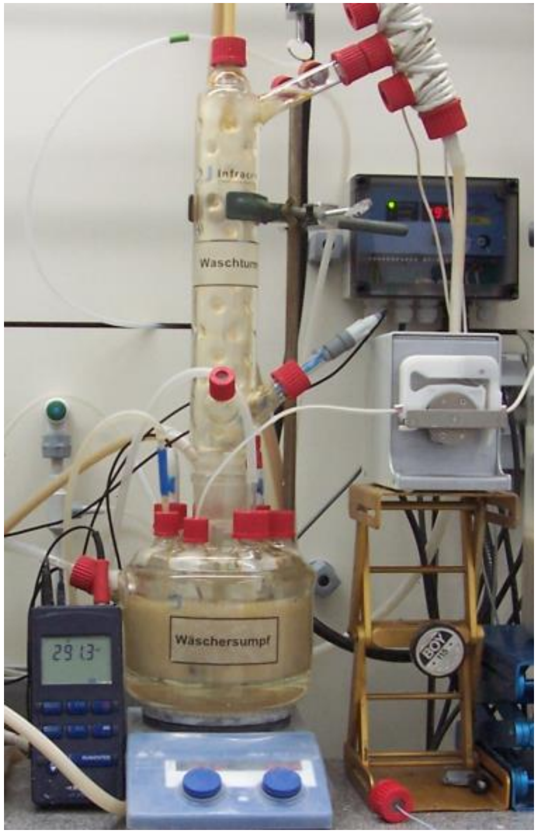
SO_2 removal efficiency: >90 %

SO_2 conc.: $\leq$ 10.000 mg/Nm³

2. Avoidance of Mercury Re-Emission

Lab-scale FGD set-up

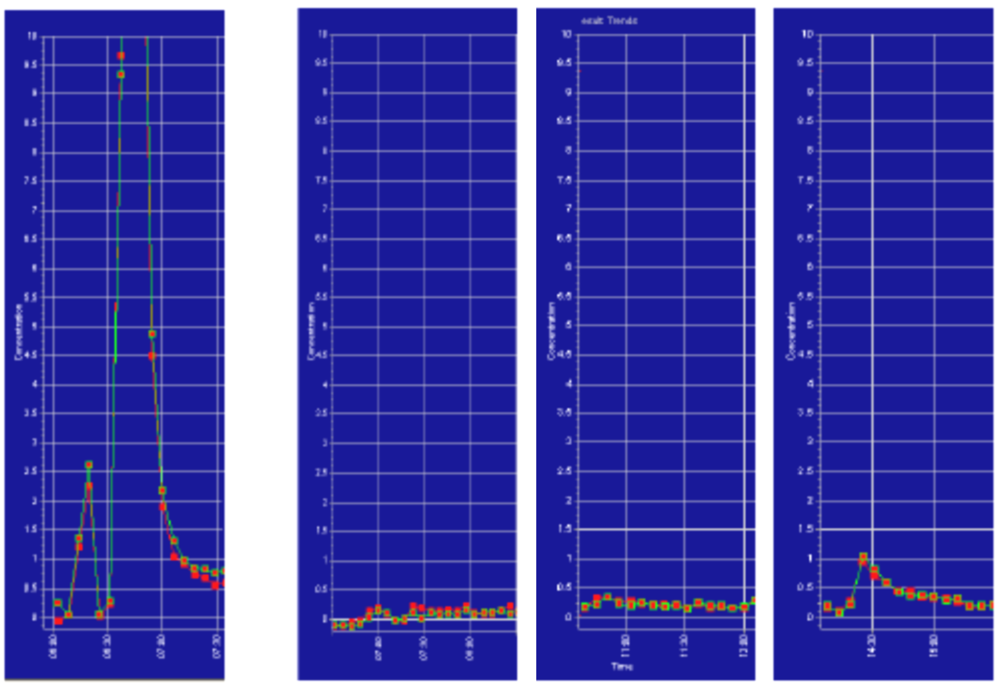




- SO_2 Raw gas
- SO_2 Clean gas
- O_2 Raw gas
- O_2 Clean gas
- N_2 Raw gas
- Oxidation-reduction potential (ORP)
- Temperature
- pH Value
- Oxidation air flow
- $Hg_{(0)}$
- $Hg_{(tot)}$

2. Avoidance of Mercury Re-Emission

Screening of different precipitation agents



Pre-trial   Precipitation agents A to C

■ Hg $_{(0)}$ ■ Hg $_{(tot)}$

- Pre-investigation by use of the lab-scale FGD on the effectiveness of precipitation agents and pre-selection of the most promising agents for the field tests.
- All investigated precipitation agents are able to reduce mercury re-emission. By use of specific precipitation agents in the lab-scale trials the $Hg_{(0)}$ emission peak which occurred during start-up with the actual suspension was also suppressed.

2. Avoidance of Mercury Re-Emission

Trials in the full-scale plant

Use of pre-selected precipitation agents in a Uniper power plant under stable operating conditions and constant load

Measurement of mercury concentrations ($Hg_{(0)}$ and Hg_{ox}) along the flue gas path, evaluation of mercury mass flows in all relevant material flows and analysis of FGD chemistry (liver test) during the trials

Share of oxidized mercury upstream of the FGD was $\geq$ 90 % during the trials

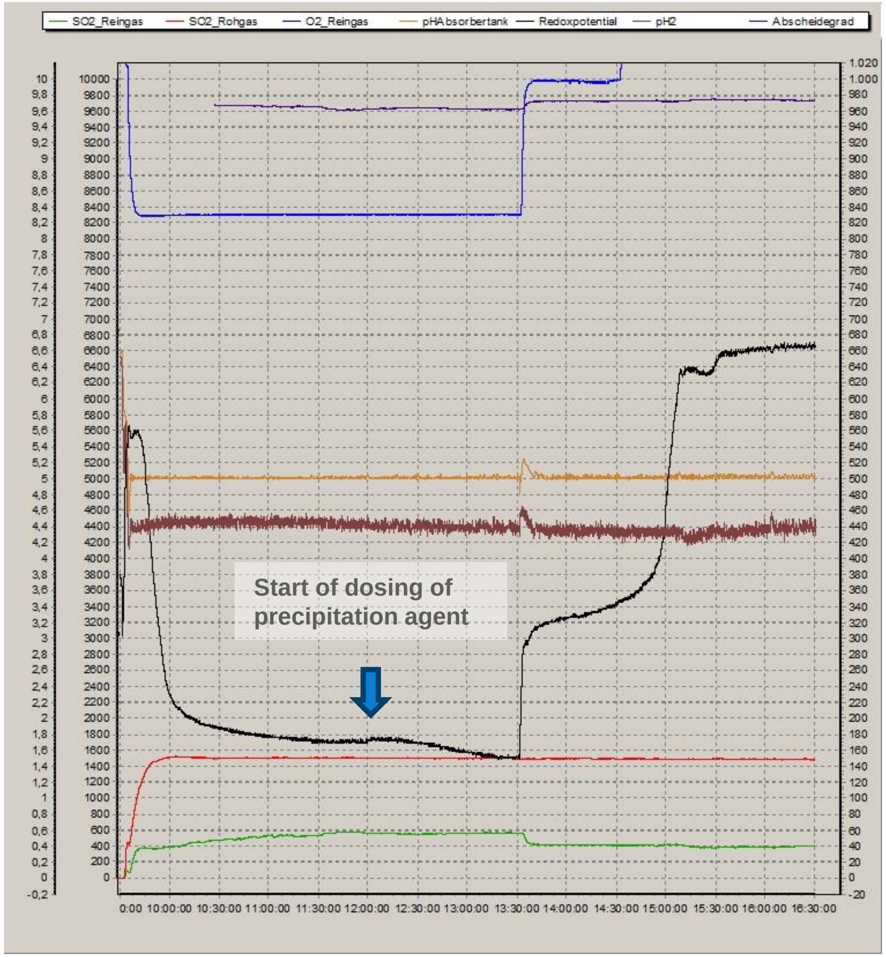
Removal efficiency for oxidized mercury of up to 97 % during use of precipitation agents can be achieved

Share of elemental mercury passes through the absorber unhindered and contributes, together with the unremoved portion of the oxidized mercury, to the clean gas emission

2. Avoidance of Mercury Re-Emission

Transfer of results from lab-scale to full-scale plants

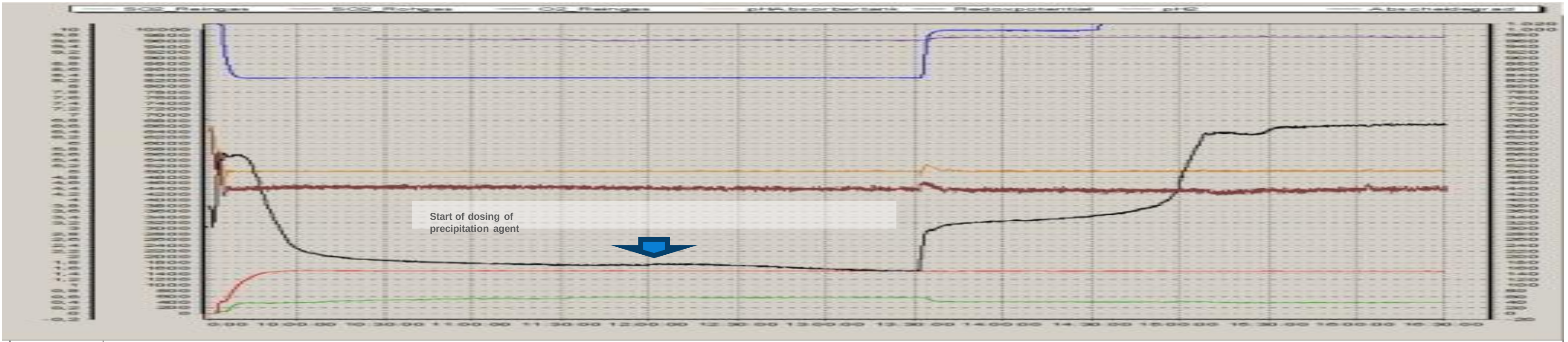
- Change of operating conditions and their impact on the mercury emissions can be simulated in the lab-scale plant.

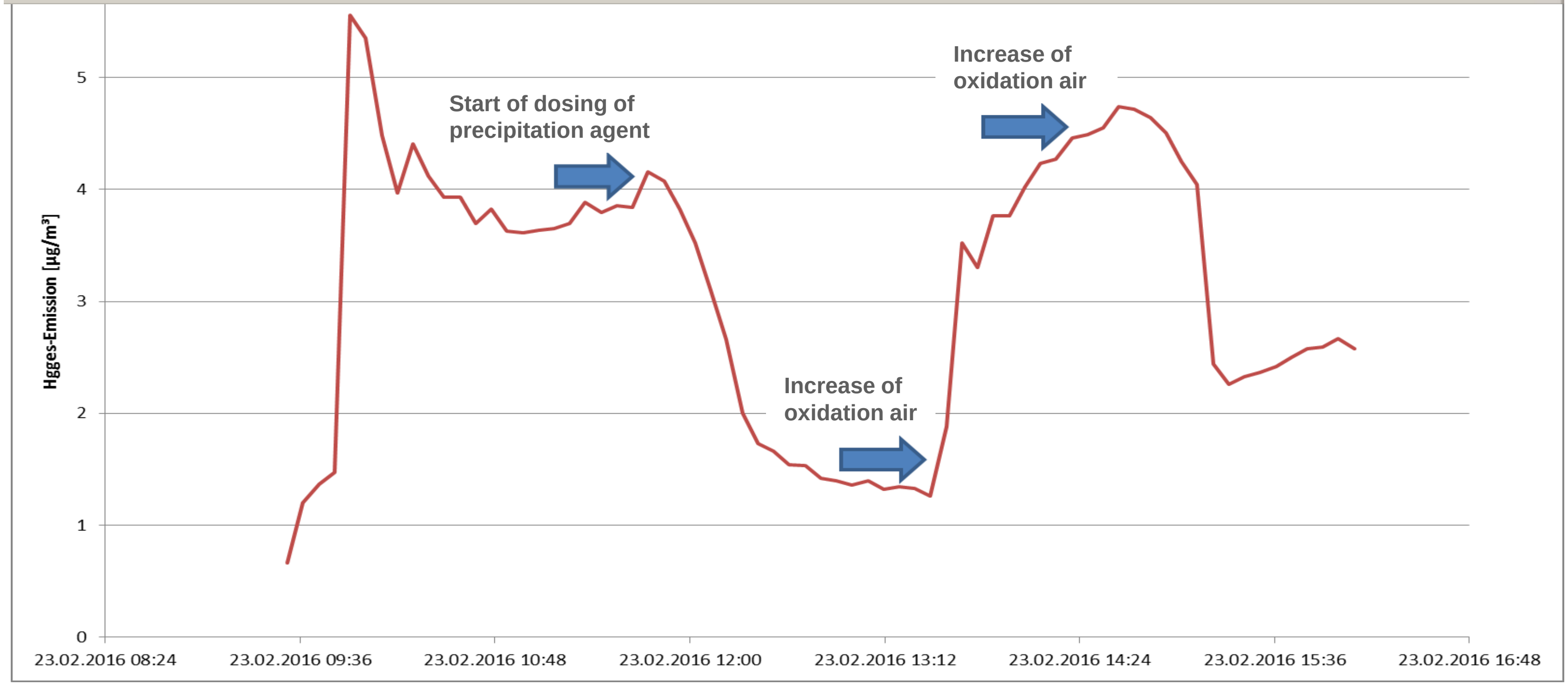


Legend

- SO_2 Raw gas
- SO_2 Clean gas
- O_2 Clean gas
- pH value sump
- pH value scrubber
- ORP

2. Avoidance of Mercury Re-Emission





2. Avoidance of Mercury Re-Emission

Liver test – the Uniper diagnostic tool for FGD

Operating status		A	B
pH value (on-site measurement)		5,1	5,2
ORP (on-site measurement)	mV	600	210
Absorber filtrate:			
Potassium (K)	mg/l	39	104
Sodium (Na)	mg/l	220	425
Calcium (Ca)	mg/l	1.120	1.180
Magnesium (Mg)	mg/l	960	835
Manganese (Mn)	mg/l	10	60
Aluminium (Al)	mg/l	4,7	3,5
Mercury (Hg)	mg/l	0,31	0,0031
Cadmium (Cd)	mg/l		0,06
Fluoride (F^-)	mg/l	32	27
Chloride (Cl^-)	mg/l	2.770	3.000
Bromide (Br^-)	mg/l	< 5	26
Iodide (I^-)	mg/l	< 5	38
Total iodine (I)	mg/l	10	45
Nitrate (NO_3^-)	mg/l	885	523
Nitrite (NO_2^-)	mg/l	0,31	2
Sulphate (SO_4)	mg/l	2.390	2.450
Sulphite (SO_3)	mg/l	< 5	< 5

Operating status		A	B
Dithionate ($S_2O_6^{2-}$)	mg/l	180	7
Peroxodisulphate ($S_2O_8^{2-}$)	mg/l	250	< 5
Thiosulfate ($S_2O_3^{2-}$)	mg/l	< 5	< 5
Amidosulphonic acid (AS)	mg/l	< 5	10
Hydroxylamine mono-sulphonic acid (HAMS)	mg/l	< 5	< 5
Hydroxylamine o-sulphonic acid (HAOMS)	mg/l	< 5	< 5
Hydroxylamine di-sulphonic acid (HADS)	mg/l	< 5	45
Hydroxylamine tri-sulphonic acid (HATS)	mg/l	< 5	75
Hydroxylamine NO-di-sulphonic acid (HAODS)	mg/l	< 5	< 5
Imidodisulphonic acid (IDS)	mg/l	< 5	40
Nitrilotrisulphonic acid (NTS)	mg/l	< 5	< 5
Sulphur (total)	mg/l	961	910
Absorber solids:	g/l	109	115
Mercury	mg/kg	0,08	2,7
Manganese	mg/kg	165	
Sulphite (SO_3)	%	< 0,02	
Calcium carbonate ($CaCO_3$)	%		
Aluminium	mg/kg	3.250	
Cadmium	mg/kg		0,11

2. Avoidance of Mercury Re-Emission

Determination of the type of sulphite oxidation by characterising the absorber suspension

Unhindered Oxidation	Hindered Oxidation
Low concentration of Iodide and SN compounds	High concentration of Iodide and SN compounds
No dissolved sulphite	Dissolved sulphite
Peroxodisulphate	Low or no peroxodisulphate
High ORP	Low ORP
Manganese mainly in the solids	Manganese mainly in the filtrate
Mercury mainly in the filtrate	Mercury mainly in the solids

2. Avoidance of Mercury Re-Emission
Impact of changing operating conditions

- Today's power plant operation is rarely at stable conditions, but is usually marked by changes in load and fuel quality. The composition of fuel and absorber suspensions varies from power plant to power plant but also within the same plant depending on the operating conditions.
- Changing operating conditions, in particular changing ORP, have a significant impact on mercury re-emission.
- Mercury emissions which have been achieved in lab-scale plants or during full-scale trials cannot be fully transferred to all operating conditions of the trial plant or to other plants.
- There is further need for research and investigation of the transition state between different operating conditions.

Thank you very much for your attention!