Mercury emission control in coal-fired power plants

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- Mercury mass flows in coal-fired power plant
- Mercury capture along the flue gas path
- Optimization of mercury removal

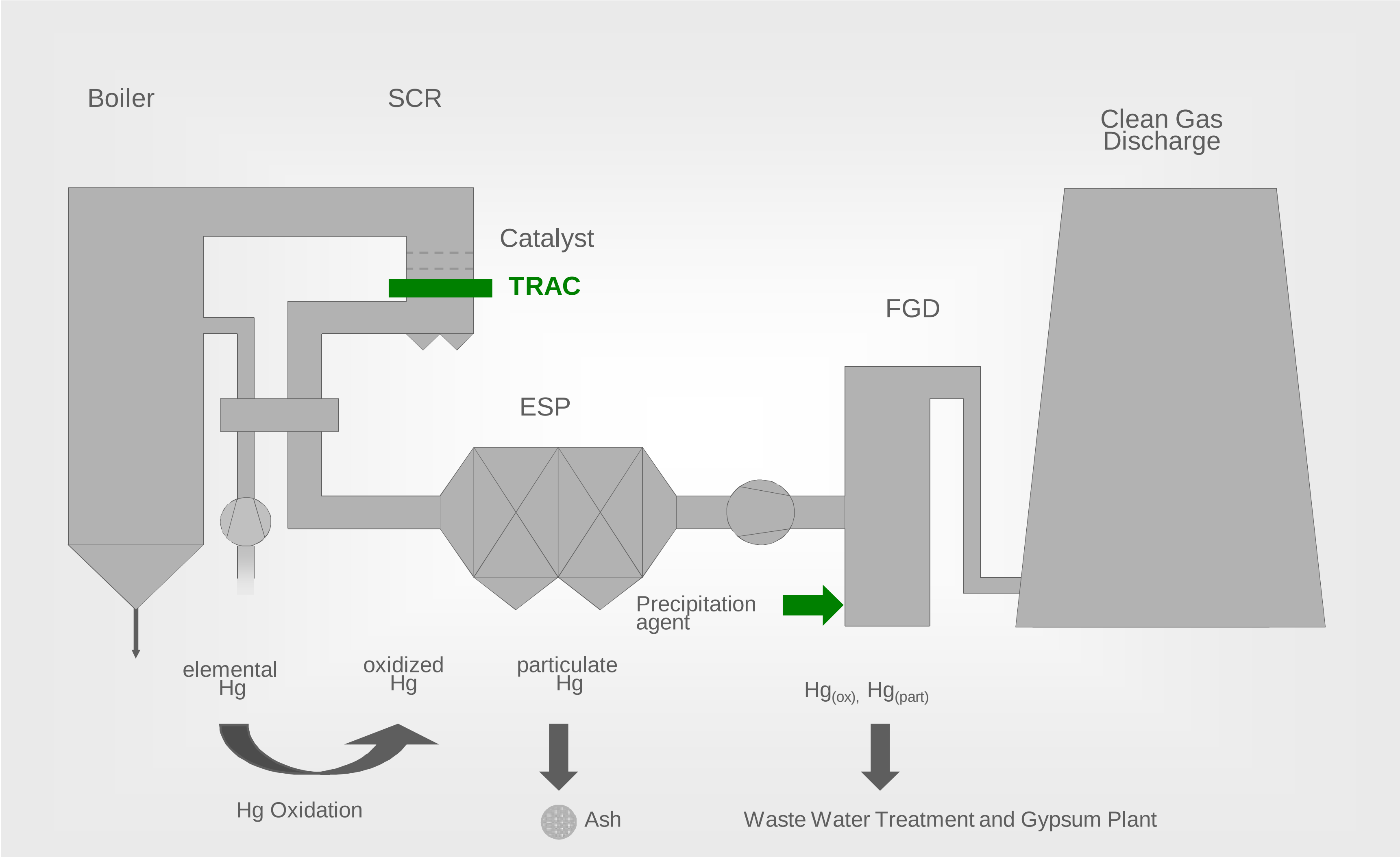
Facts about Mercury

Name	Mercury
Chemical Elemental Symbol	Hg from Hydrargyrum (hydor = water; argyros = silver)
Occurrence	to 10^{-5} % in the earth's crust in the form of 7 stable isotopes (Number 62 in the list of the most common elements)
Properties	The only metal and with Bromine, the only elements which are liquids under normal conditions (Melting point: -38.8 ° C, Boiling point: 356.7 ° C)
Hazard symbols	

Physical and chemical properties of Mercury

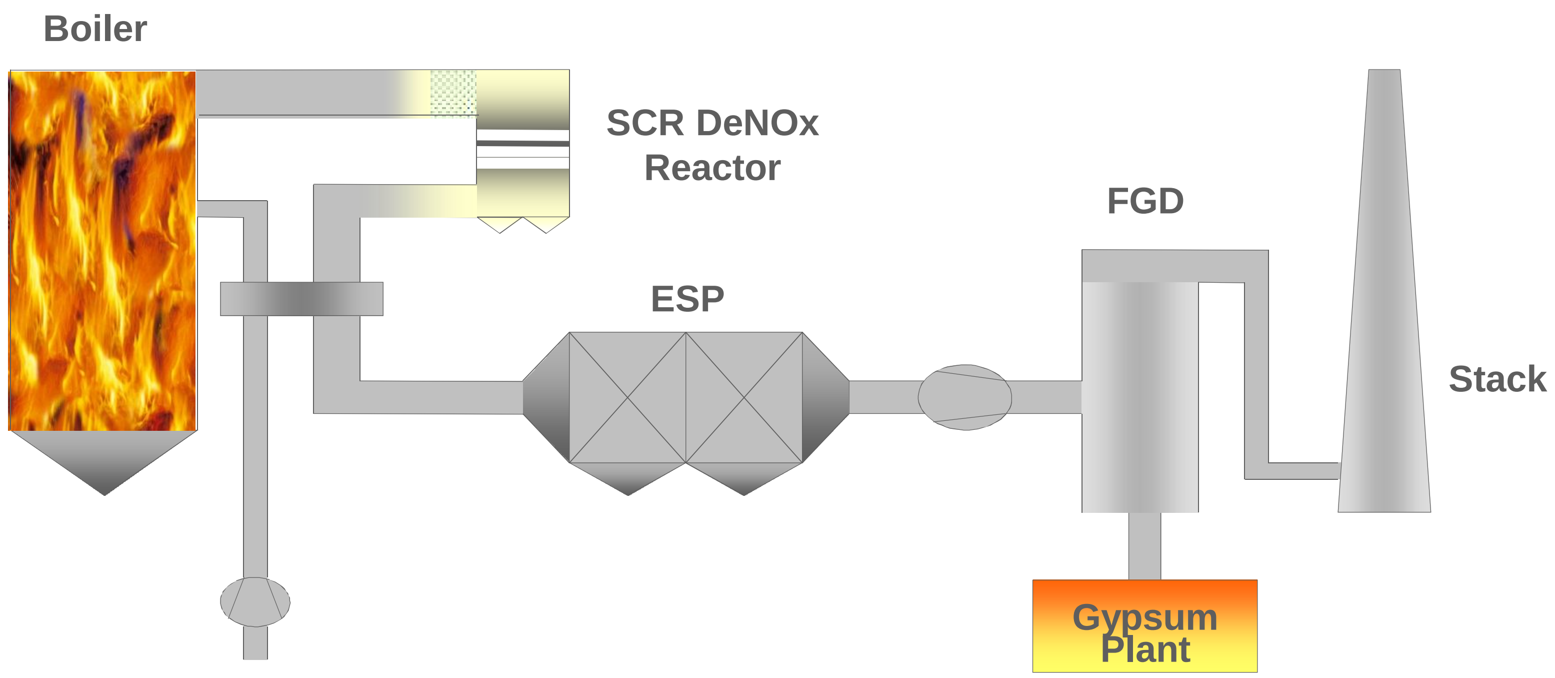
- Has a relatively high vapor pressure (0.16 Pa at 293 K)
- Exits in three oxidation states: 0, +I and +II
- In the oxidation state (+I), forms low-soluble compounds (Hg_2Cl_2 calomel)
- In the oxidation state (+II), forms very-soluble (Hg_2Cl_2 sublimate) and very slightly soluble (HgS cinnabar) compounds
- Forms with a variety of ligands complexes (for example, $[HgCl_4]^{2-}$, $[HgBr_4]^{2-}$, $[HgJ_4]^{2-}$)
- Forms organic compounds (such as methyl mercury $H_3C\text{-}Hg^+$)

Mercury mass flows in coal-fired power plant



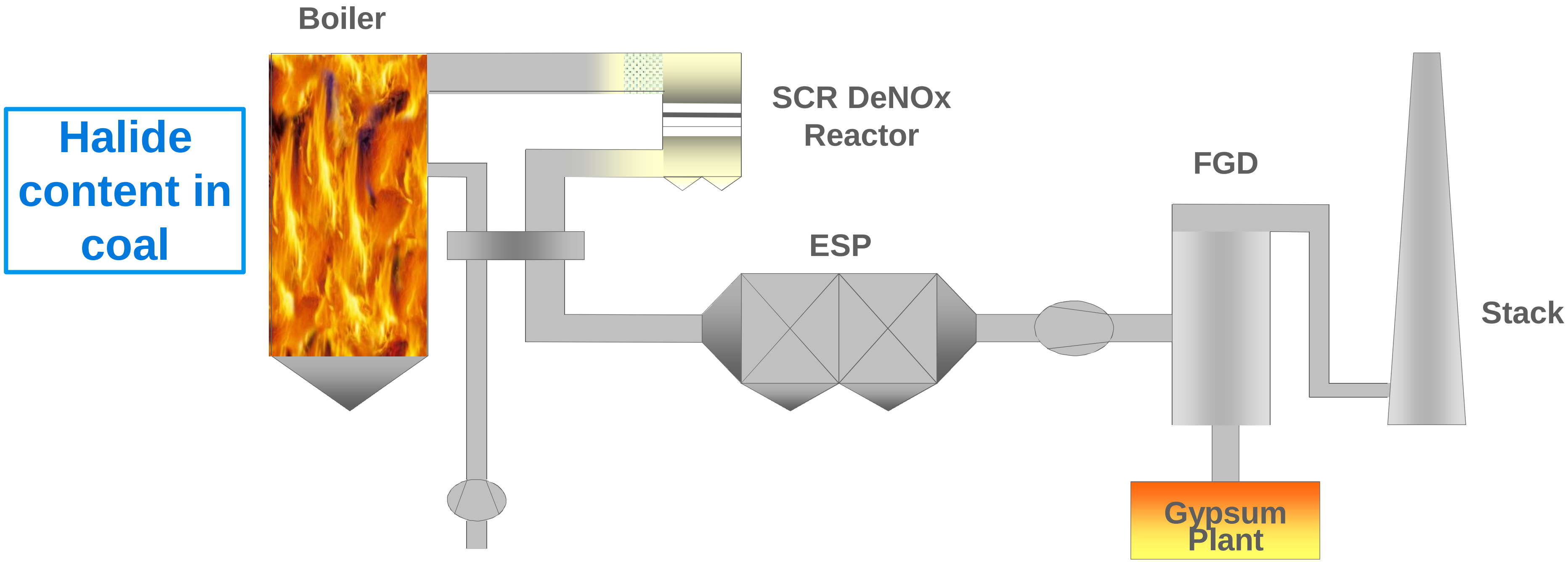
Mercury capture along the flue gas path

- Mercury is transferred completely into the gas phase by combustion
- Mercury occurs in elemental and oxidized form
- Oxidized mercury can be more easily separated in the FGD unit



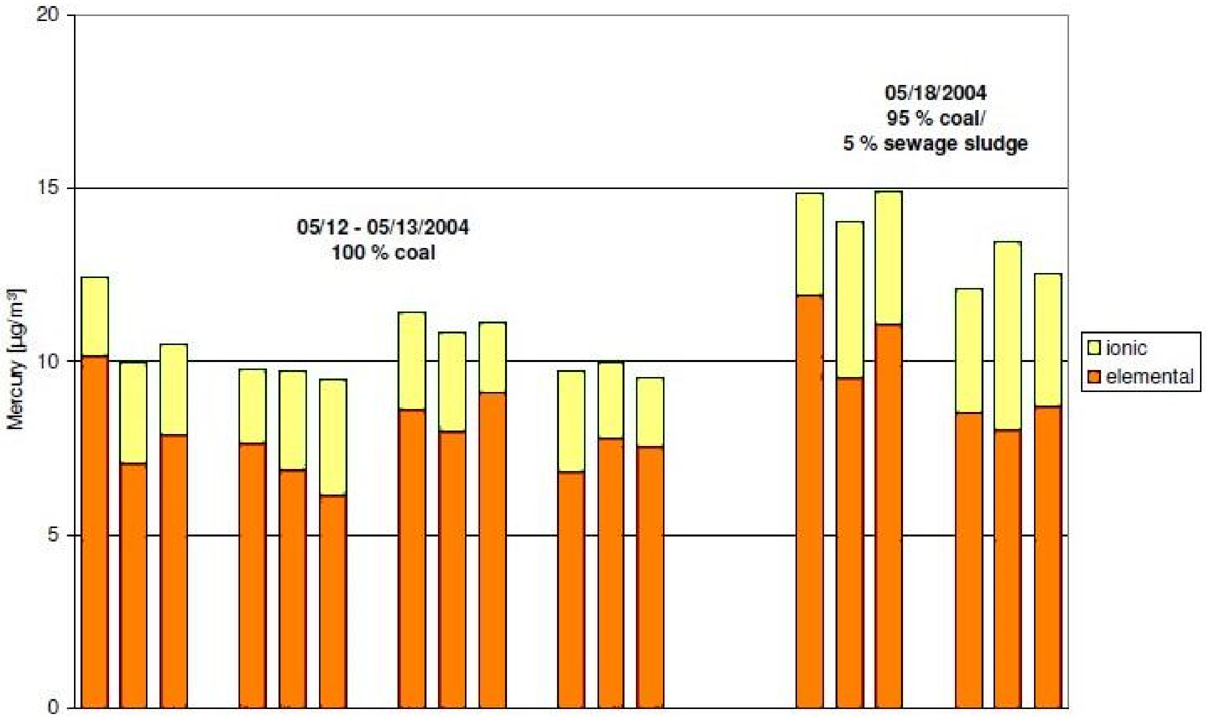
Mercury in boiler

- **Important factors:**



Mercury in boiler

- **After the boiler, is still predominantly metallic mercury**

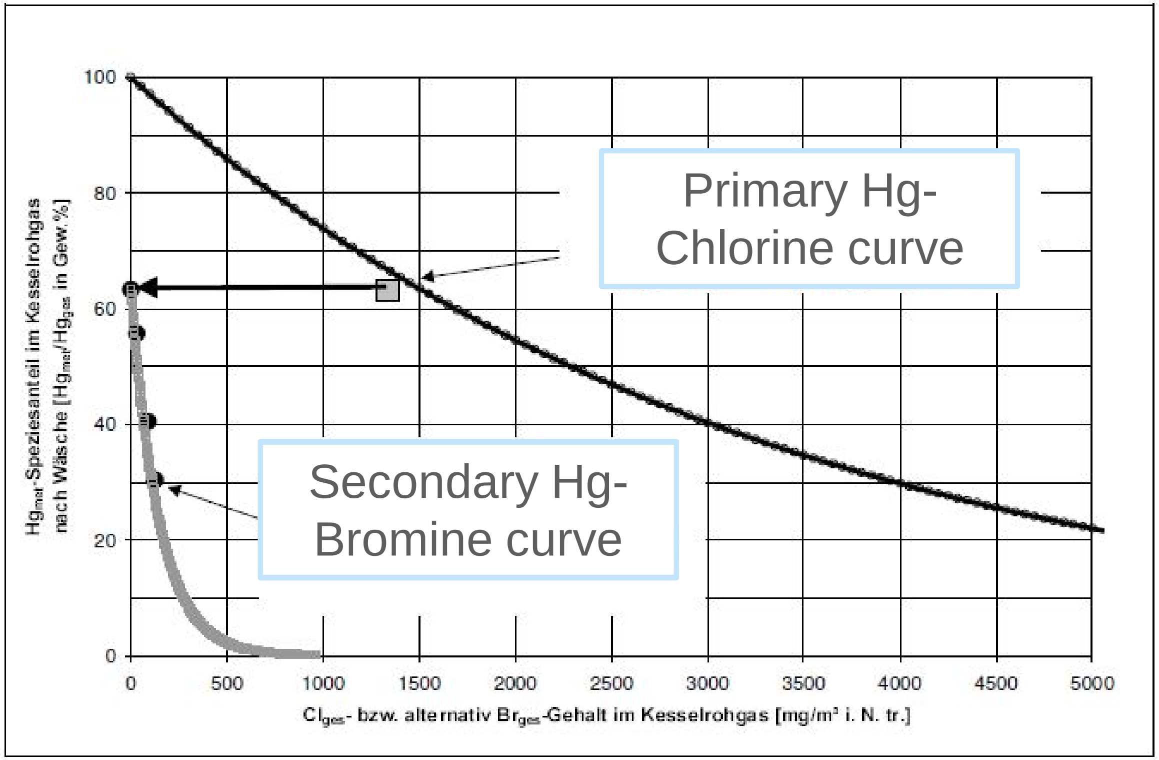


Measurements by discontinuous Dowex® / iodized active carbon adsorption

- Alternative fuels can provide additional Hg input
- The ratio elemental/ionic mercury is determined by the flue gas composition

Mercury in boiler

- **Patented process for bromine-aided mercury separation**



Hg halogenation curves by Vosteen and Kanefke

- The Hg oxidation occurs mainly through intermediate chlorine and bromine

$$4\,HCl + O_2 \leftrightarrow 2\,H_2O + 2\,Cl_2$$

(Deacon Reaction)

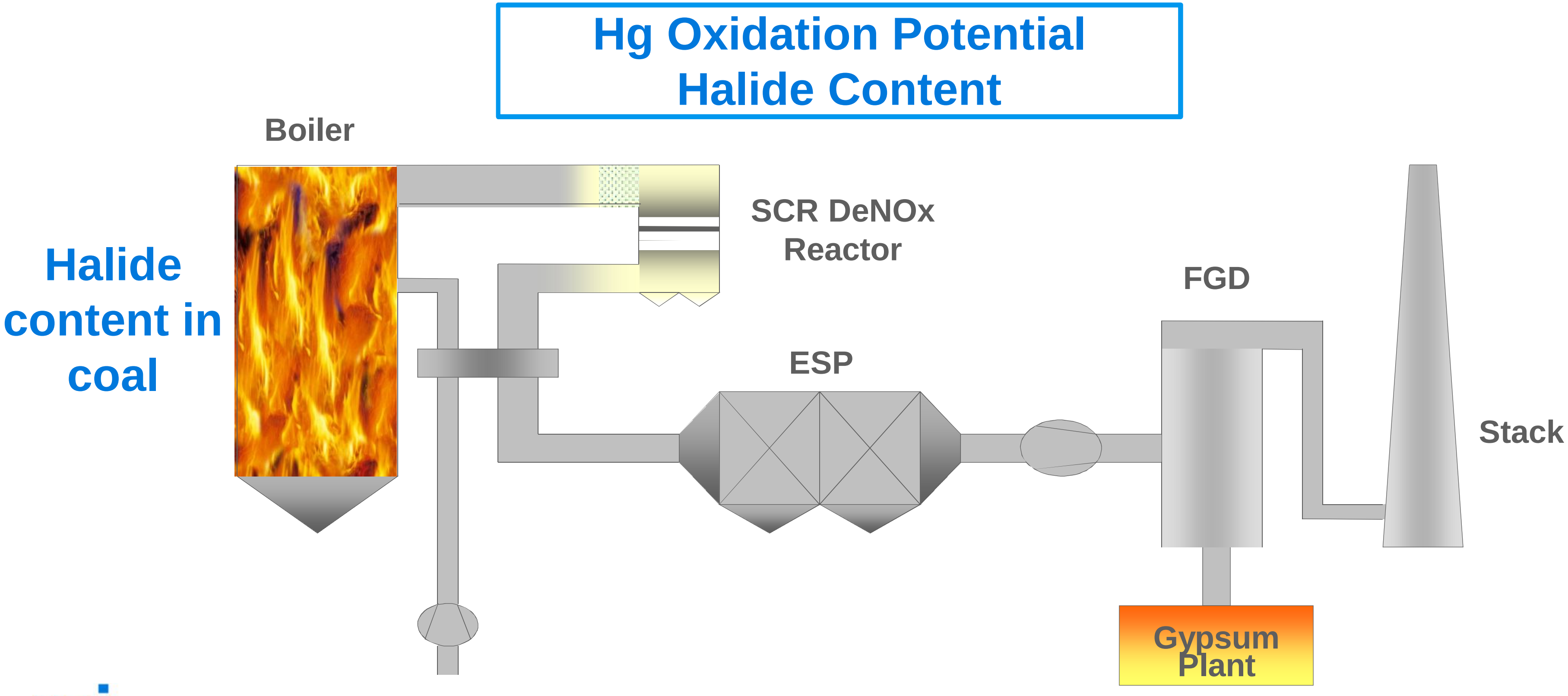
- Bromine is many times more effective than chlorine, since chlorine is also consumed by SO_2

$$SO_2 + Cl_2 + H_2O \leftrightarrow SO_3 + 2\,HCl$$

(Griffin Reaction)

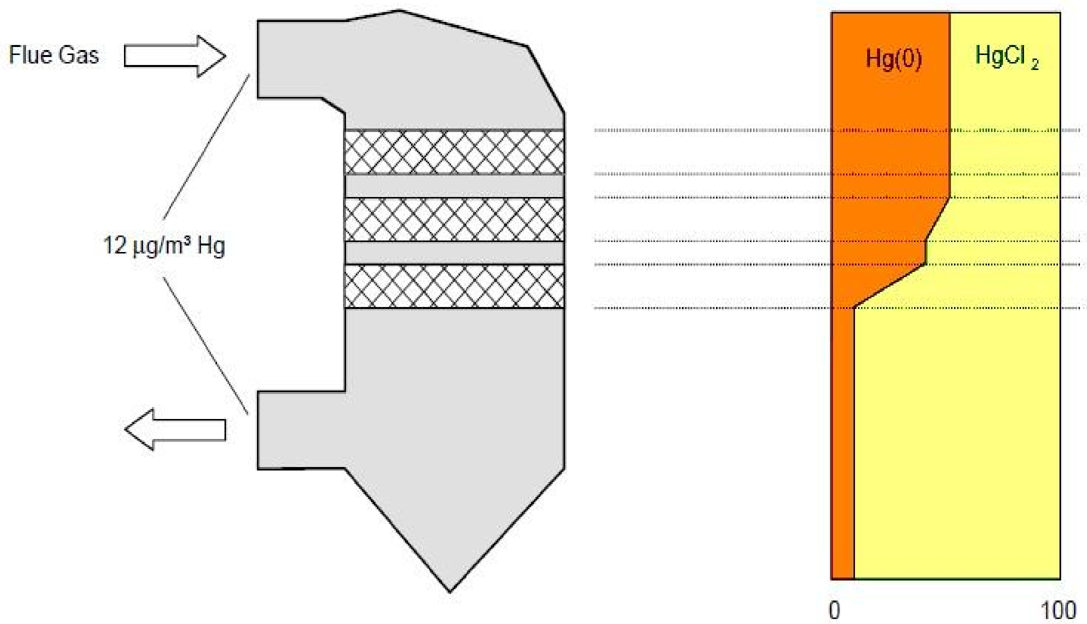
Mercury in the SCR DeNOx Reactor

- **Important factors:**



Mercury in the SCR DeNOx Reactor

- **A parallel reaction in addition to DeNOx reaction and SO_2 conversion**



- The Hg oxidation takes place mainly in the last catalyst layer
- The presence of halides is required
- Economizer and thermal wheel can be catalytically effective

Oxidized mercury can be easily precipitated in the FGD system

Mercury in the SCR DeNOx Reactor

- **A first-order reaction**

Hg-Oxidation rate: $$\eta_{Hg} = \frac{c_{Hg^{el}_{ein}} - c_{Hg^{el}_{aus}}}{c_{Hg^{el}_{ein}}}$$

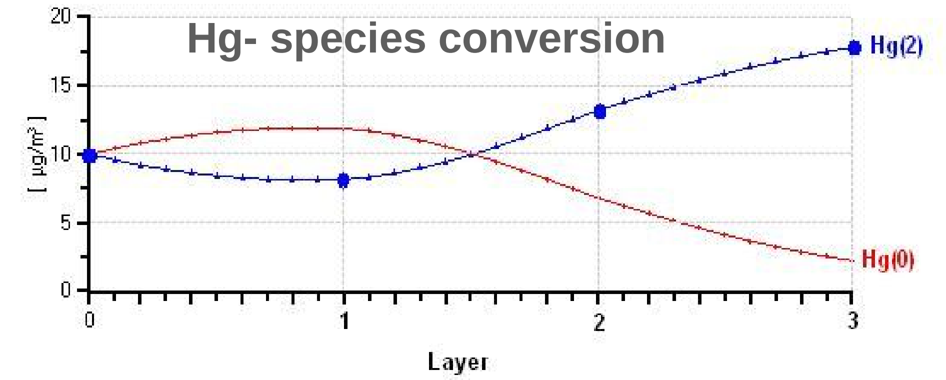
Hg Activity [m/h]: $$K_{Hg} = -AV * \ln(1 - \frac{c_{Hg^{el}_{ein}} - c_{Hg^{el}_{aus}}}{c_{Hg^{el}_{ein}}})$$

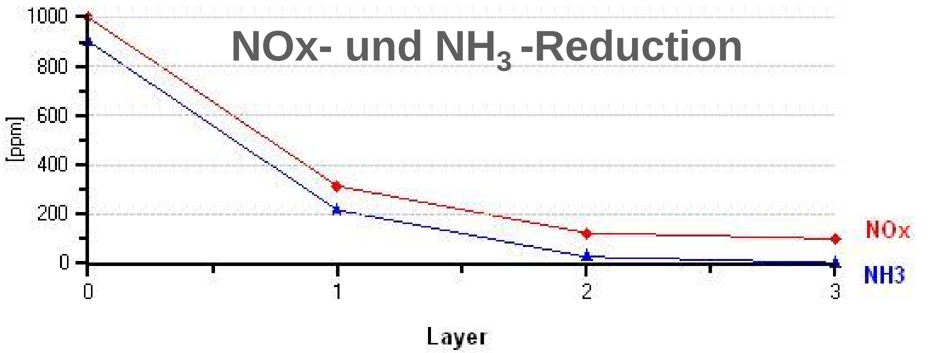
$$K_{Hg} = -AV * \ln(1 - \eta_{Hg})$$

- Hg oxidation and SO_2 conversion take place at the same active centers
- Hg reduction is also possible if ammonia concentration is still high (first catalyst layers)

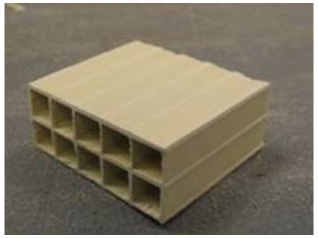
Mercury in the SCR DeNOx Reactor

- **Model Simulation**





- At high NOx and NH_3 concentrations , Hg reduction takes place
- Other factors affecting the Hg-oxidation:
  - Catalyst geometry
  - Chemical composition, esp. V content
  - Temperature
  - Flue gas composition



Mercury in the SCR DeNOx Reactor

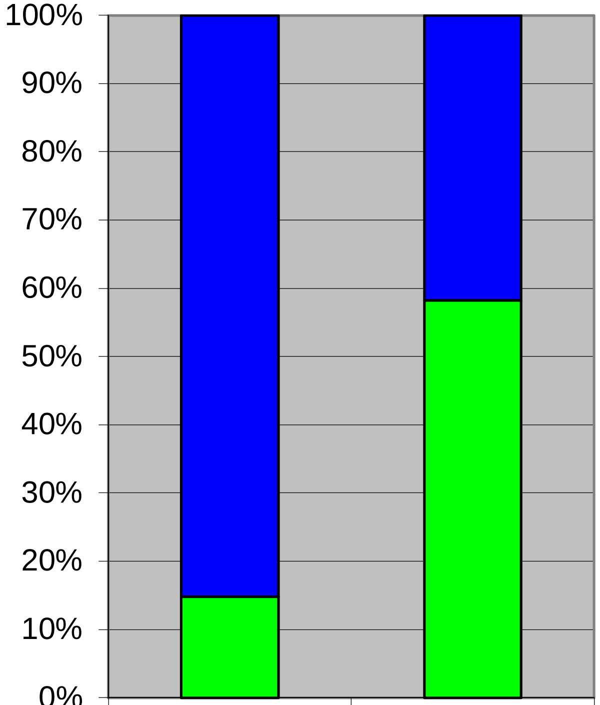
- **Use of a TRAC catalyst**

- 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 (Germany)
- 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)

Mercury in the SCR DeNOx Reactor

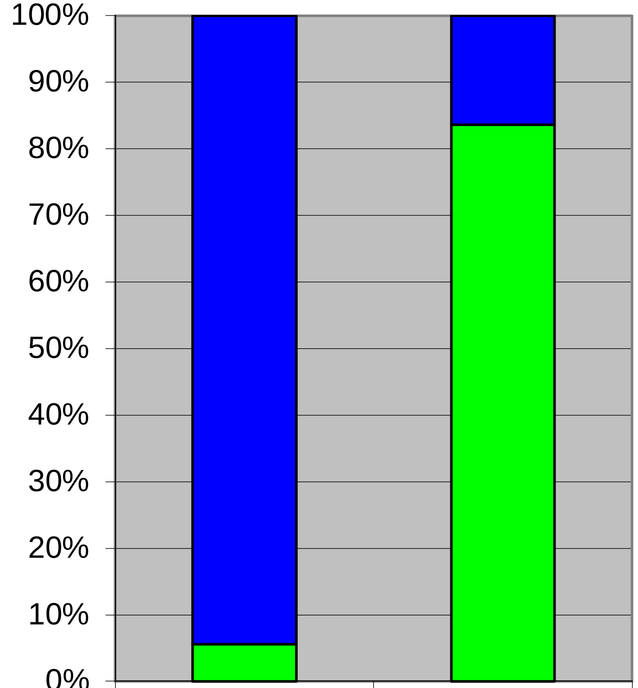
- **Mercury oxidation across the SCR plant**

before Installation of TRAC



	upstream SCR	downstream SCR
Hg (0) in %	85.2	41.8
Hg (ox) in %	14.8	58.2

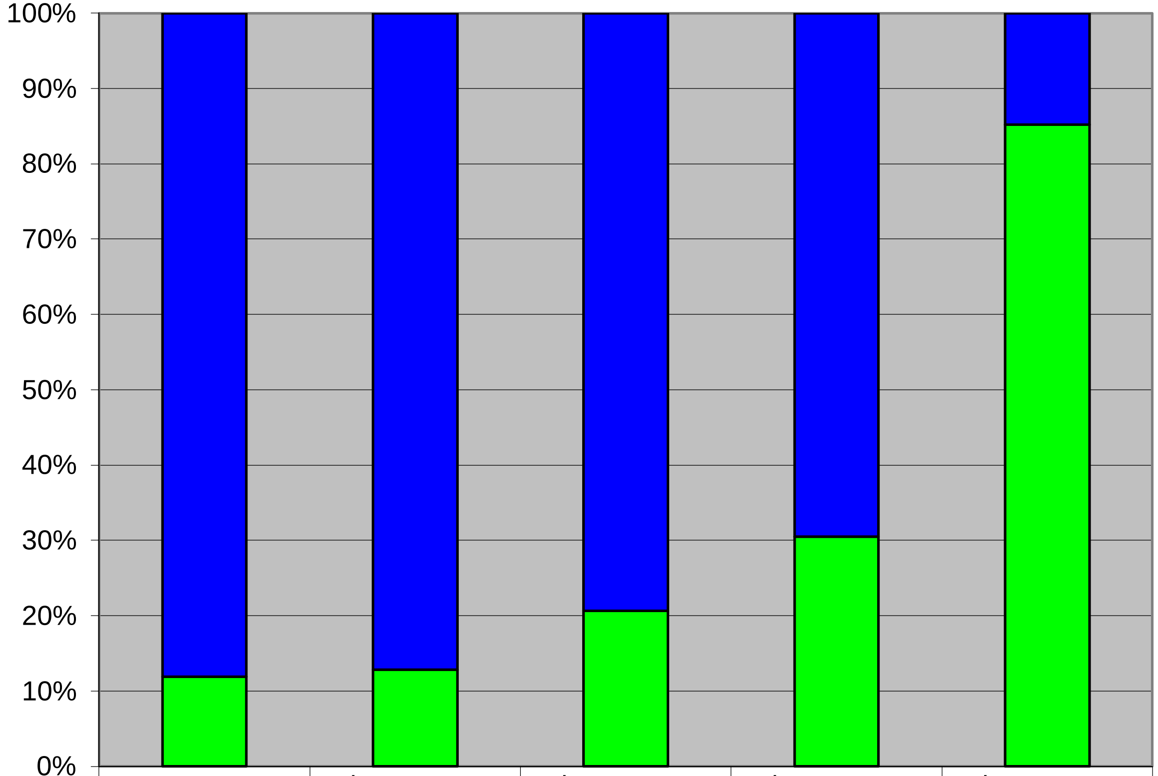
after installation of TRAC



	upstream SCR	downstream SCR
Hg (0) in %	94.4	16.4
Hg (ox) in %	5.6	83.6

Mercury in the SCR DeNOx Reactor

- **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

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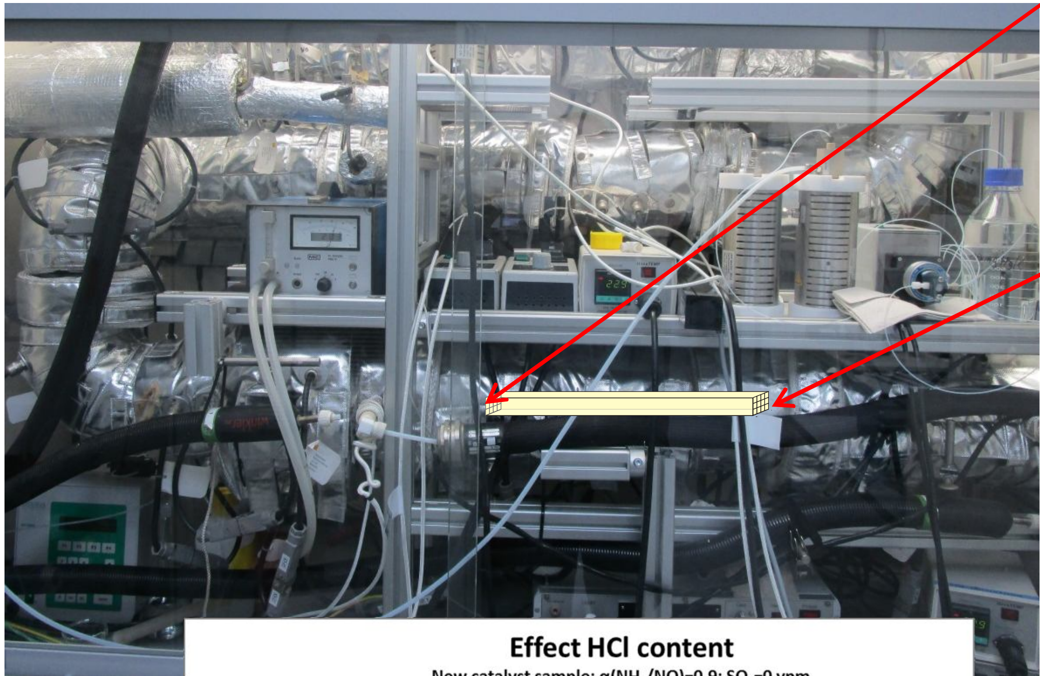
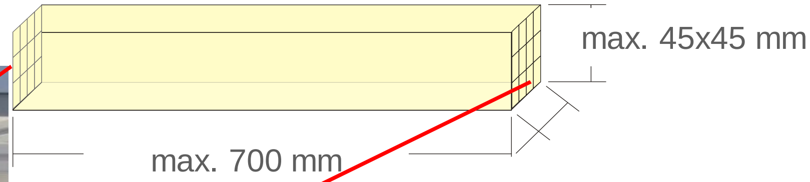
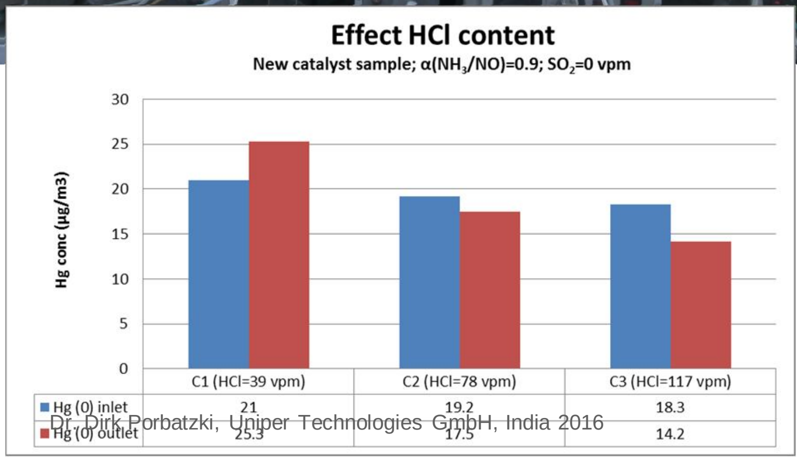
Mercury in the SCR DeNOx Reactor

- **Semi-bench scale SCR reactor**



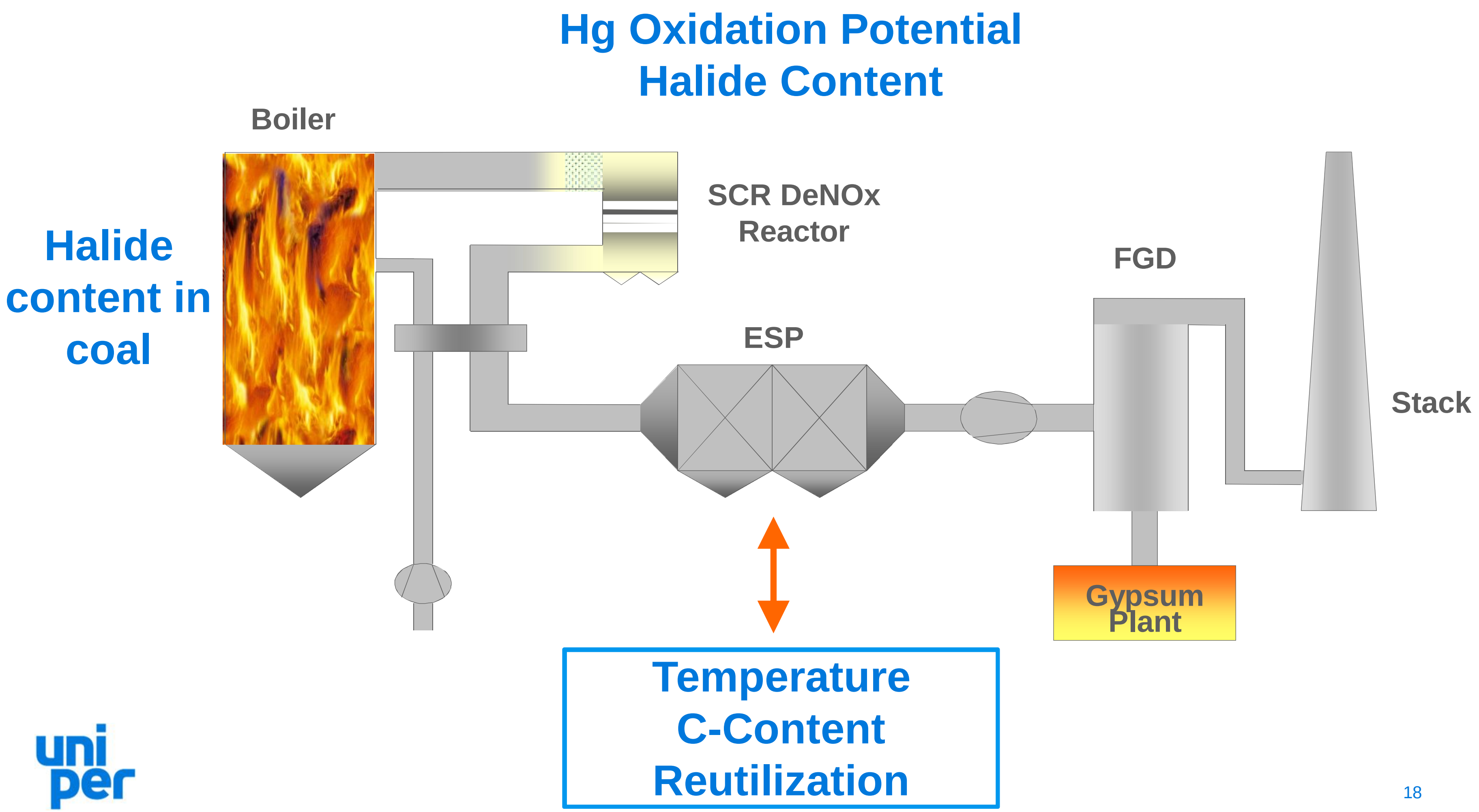




- Operation of a semi-bench scale reactor for measurement of mercury oxidation since 2013
- Comparison of different catalysts under
  power plant conditions
- Investigation of the impact of temperature and flue gas composition (Cl, SO_2, NH_3,...) on mercury oxidation activity
- Simulation of different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

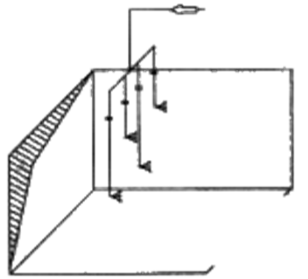
Mercury in the ESP

- **Important factors:**



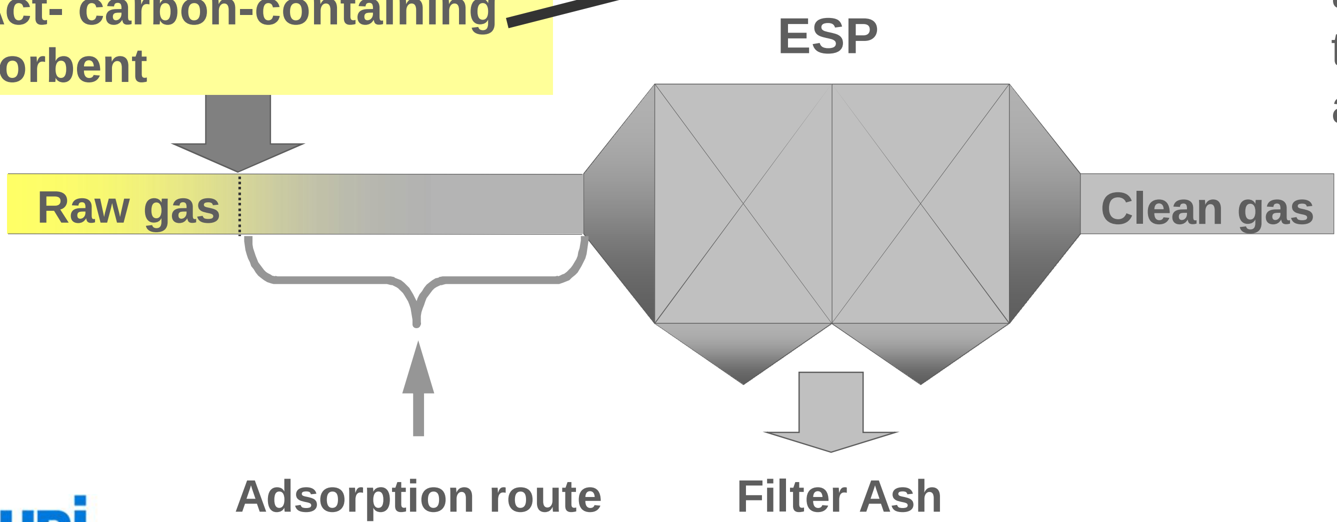
Mercury in the ESP

- **Effectiveness of air power absorbers**



- **Mineral Adsorbents**
- **Act- carbon-containing sorbent**

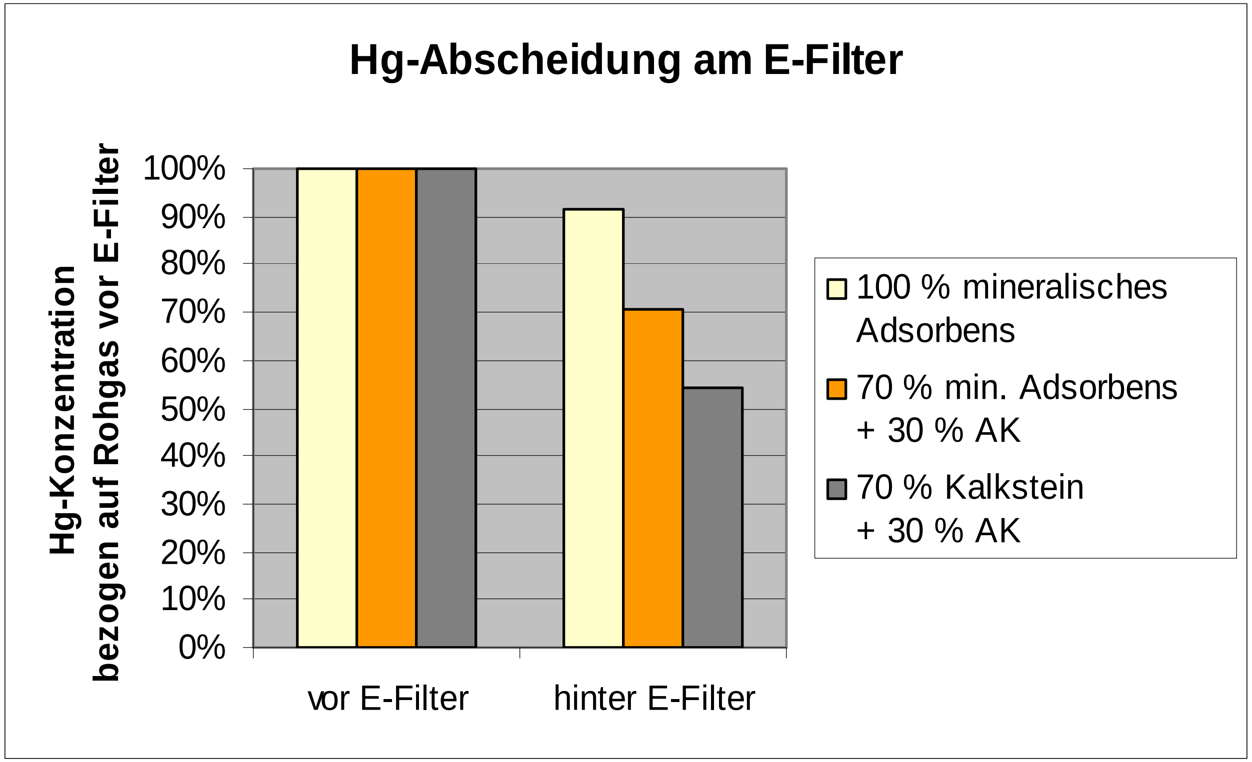
Ex-Protection must be considered



- Filter temperature influences the choice of the adsorbent
- Influence on the ash quality is taken into account.

Mercury in the ESP

- **Effectiveness of adsorbents**



- Pure mineral absorbents show only a limited effect
- The presence of H_2SO_4 promotes Hg deposition
- Separation rates to 60% with filter temperatures of 120°C

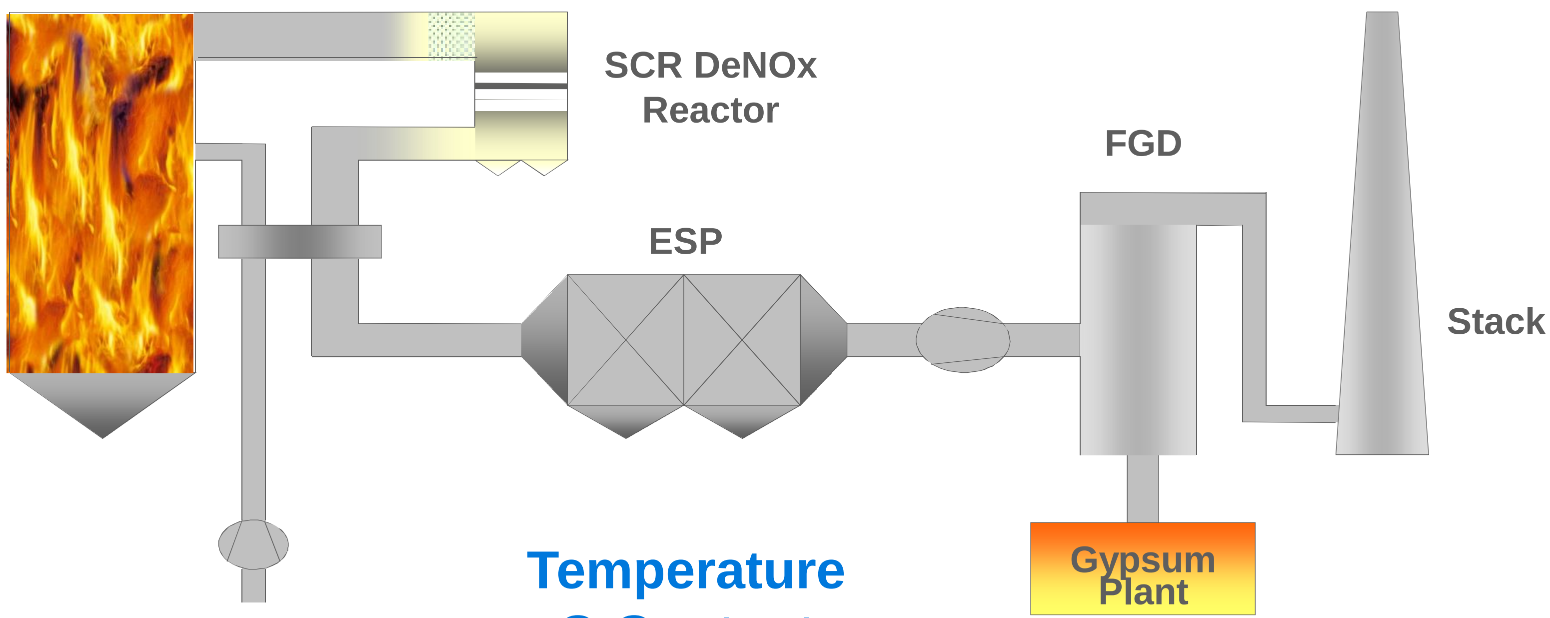
Mercury in the FGD

- **Important factors:**

Hg(0)/Hg(ox)
Halide content
Operating state changes
Precipitating agent

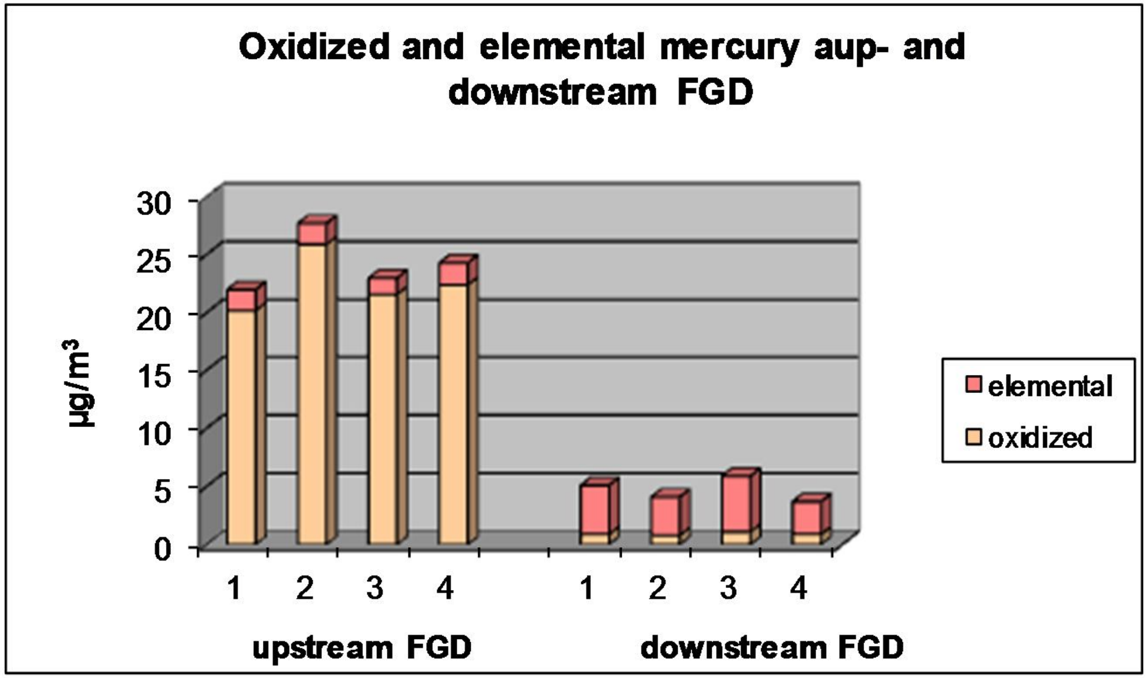
Hg Oxidation Potential
Halide Content

Halide content in coal



Temperature
C-Content
Reutilization

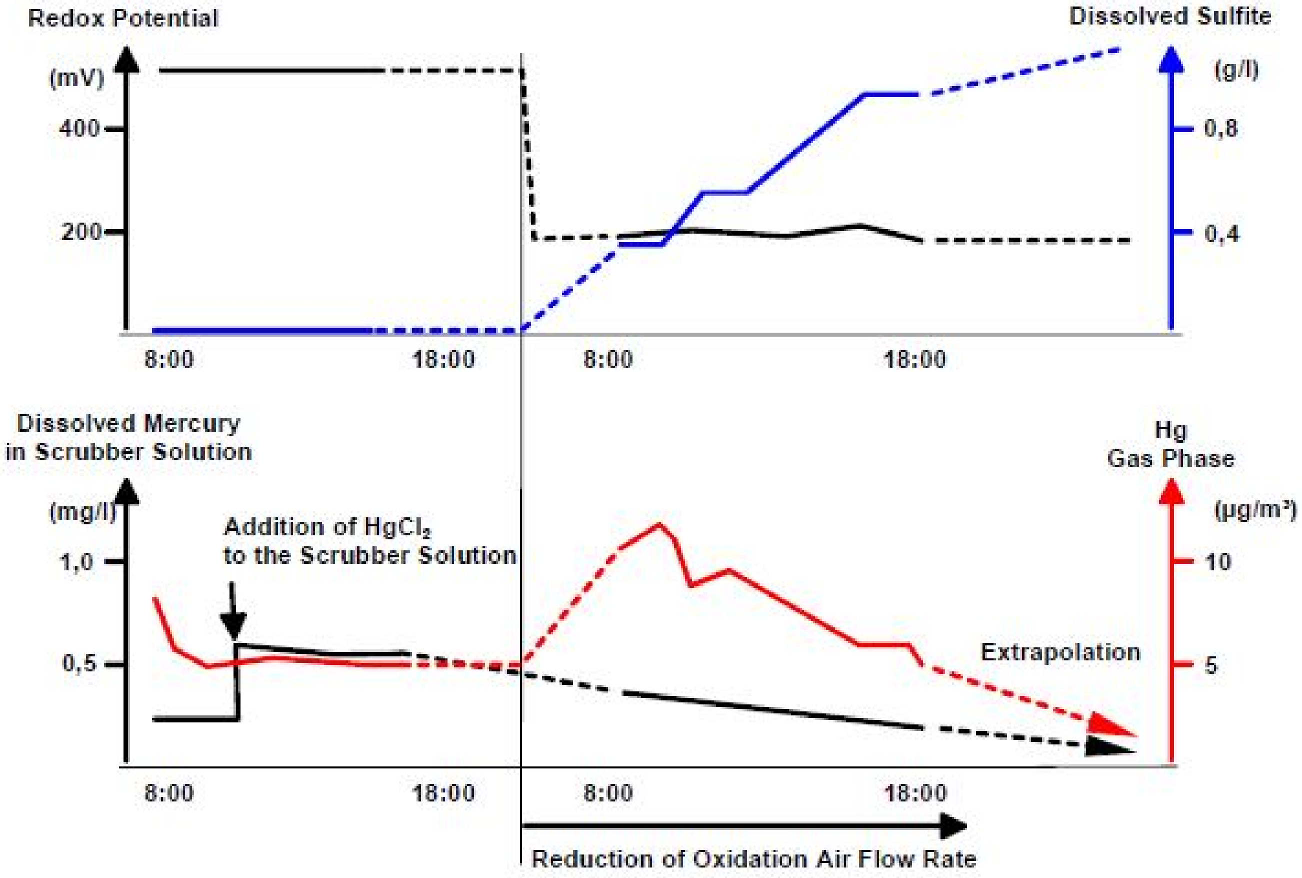
Mercury in the FGD



- Oxidized Hg can be generally good separated in wet scrubbers.
- Metallic Hg passes generally through the FGD scrubber.
- Re-emissions by Hg(ox) reduction or formation of volatile Hg compounds, such as HgJ_2, is possible.

Mercury in the FGD

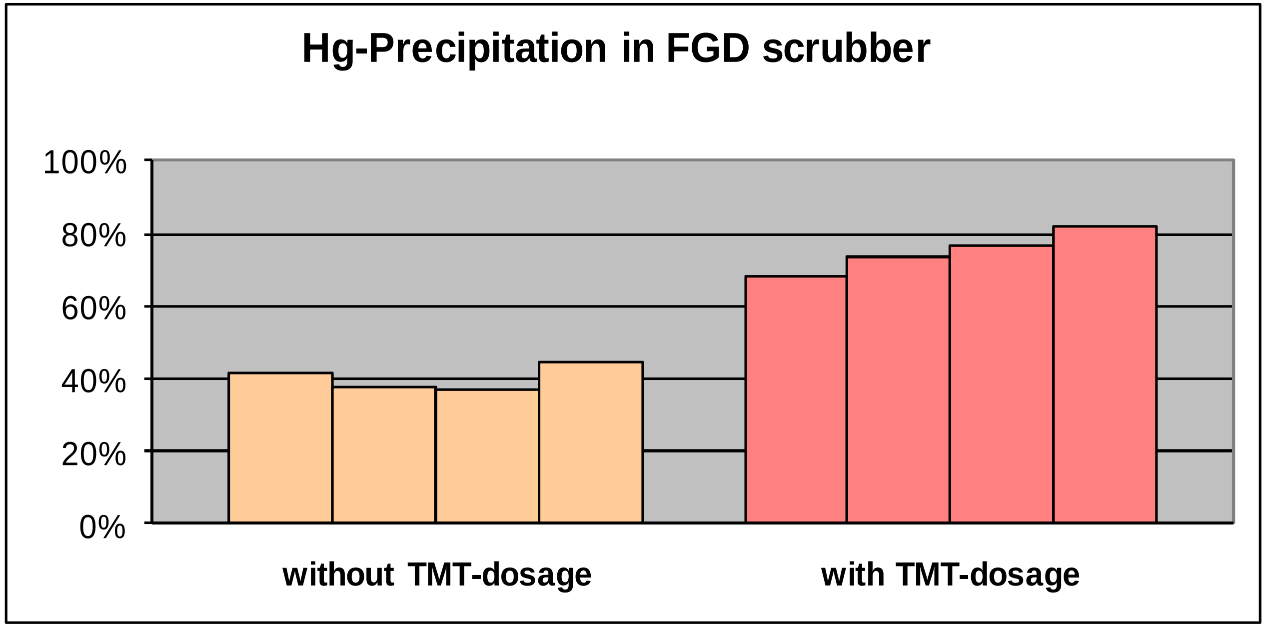
- **Operating state changes can lead to significant re-emission from the FGD**



- **Laboratory test:** lowering the redox potential by reducing the oxidation air
- Low redox potential → Hg in solid compounds → sulfit formation → lowered SO2 precipitation
- High potential → possibly dark color of gypsum → Mn-Oxides and Cl2 formation

Mercury in the FGD

- **Effectiveness of precipitant agents**



- Inorganic sulfidic precipitant and activated carbon are also effective.
- Influence on the gypsum quality is taken into account.

Mercury in the FGD

- **Impact of changing operating conditions**

  - Today's (european) 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.

  - Mercury emissions which have been achieved in lab-scale plants or during full-scale trials cannot be transferred automatically to all operating conditions of the trial plant or to other plants.

Optimization mercury removal

- Halides improve the mercury oxidation in the boiler.
- Special Hg oxidation catalysts increase the oxidation rate.
- Additive dosage before ESP enables improved deposition with the fly ash.
  Caution! Ash quality may be affected.
- Mercury separation in the FGD is favored by high chloride content.
- Precipitant agents improve additionally the separation.
  Caution! Gypsium quality may be affected.
- Operating condition changes may trigger significant mercury emission peaks.


Questions

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Mercury in the FGD

- **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

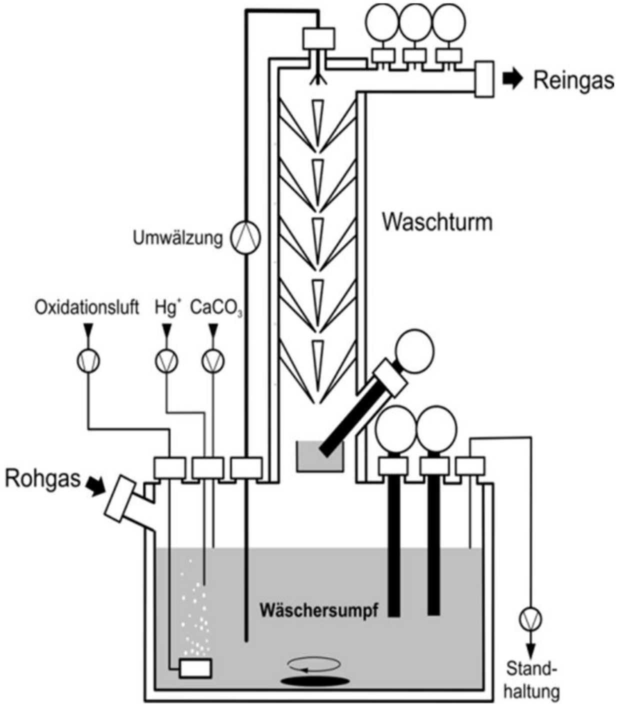
Mercury in the FGD

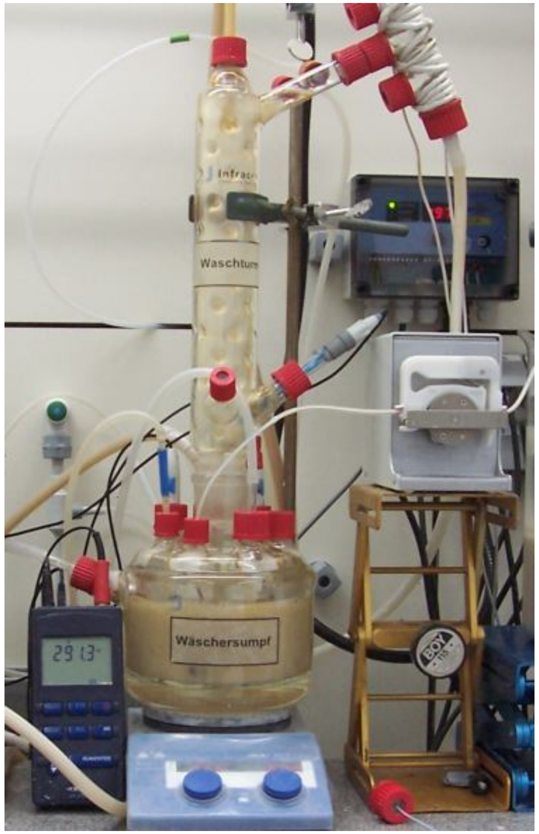
- **Use of the UTG lab-scale FGD**

- Used for investigation of mercury mitigation and 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.

Mercury in the FGD

- **Lab-scale FGD set-up**

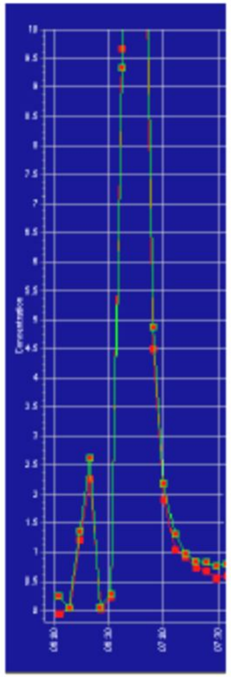




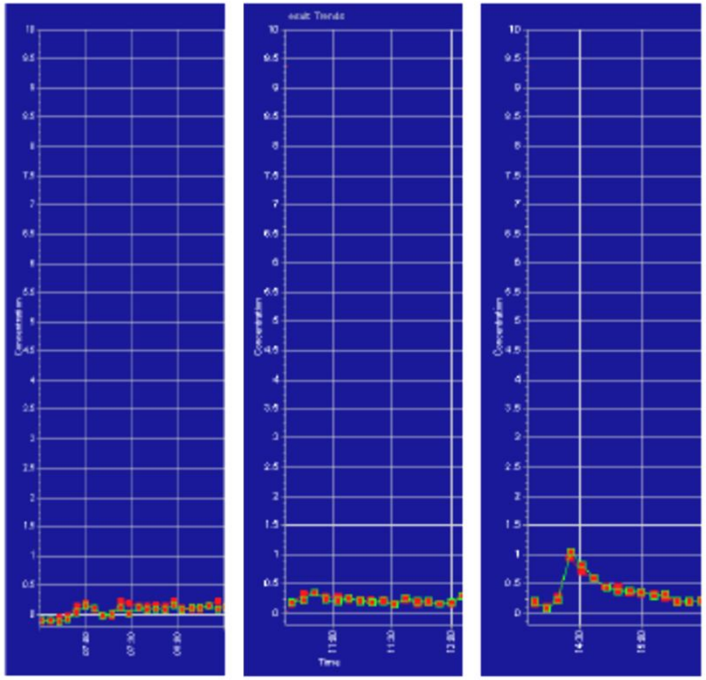
- SO_2 Raw gas
- SO_2 Clean gas
- O_2 Raw gas
- O_2 Clean gas
- N_2 Raw gas
- Oxidation-reduction potential (ORP)
- Temperature
- pH Value
- Oxidation air flow
- $Hg_{(0)}$
- $Hg_{(tot)}$

Mercury in the FGD

- **Screening of different precipitation agents**



Pre-trial



Precipitation agents A to C

- 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.

▪ $Hg_{(0)}$ ▪ $Hg_{(tot)}$

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