Reinhold Environmental Ltd.

2007 APC Round Table & Expo Presentation

July 8-10, 2007
Chattanooga, TN
Hosted by TVA

Selective Separation of Mercury and Other Heavy Metals During FGD Wastewater Treatment

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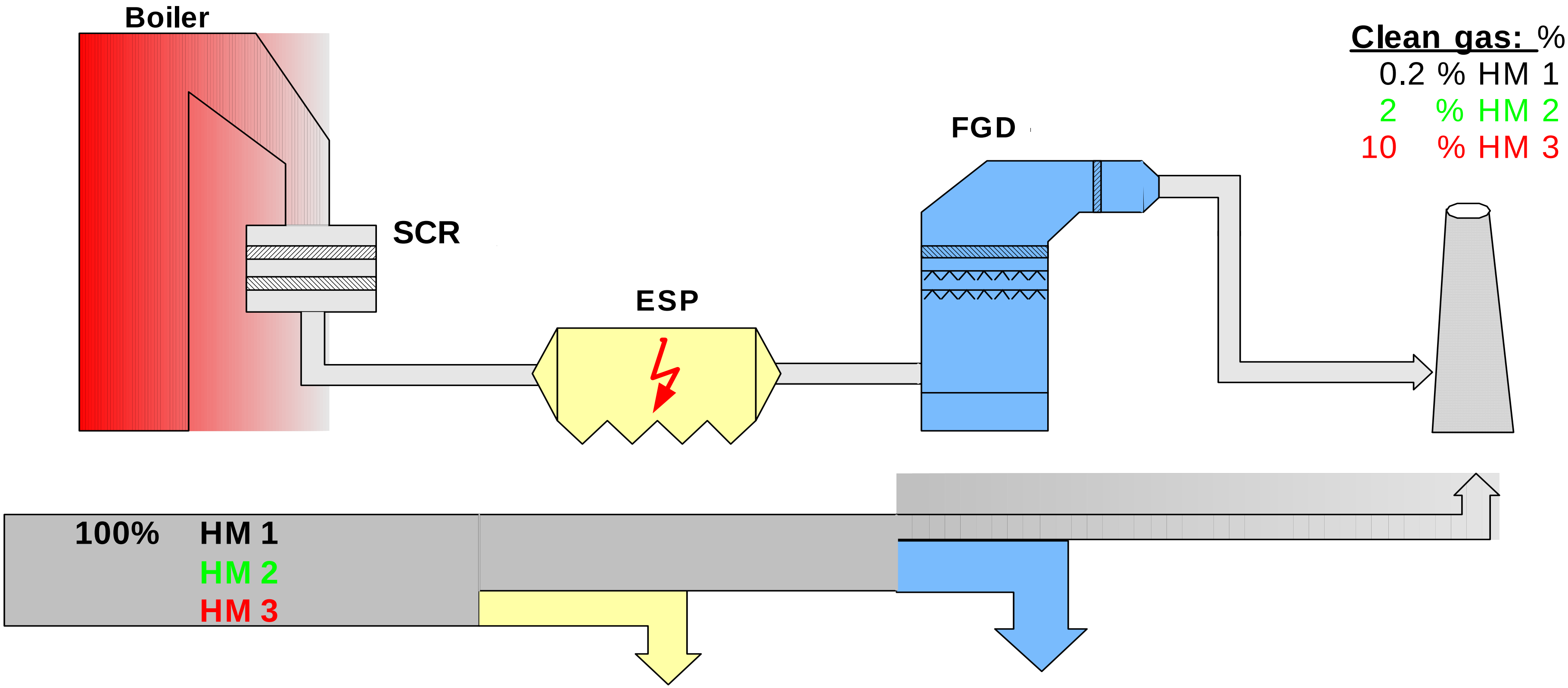
The Search for FGD Wastewater Treatment Options

- **Dilemmas Faced by Operators:**
  - **Estimation on FGD wastewater composition**
  - **Various plants using a variety of fuels and different FGD designs**
  - **Dealing with different water supply qualities**
  - **Various effluent discharge requirements**

The Search for FGD Wastewater Treatment Options

- **Goals for Operators:**
  - **Investigate a range of proven wastewater treatment processes**
    - **Simple sedimentation and clarification systems to extensive metal treatment systems**
  - **Establish strategies for treatment implementation**
- **Steag provides:**
  - **Over 25 years experience with operating FGD systems and managing their wastewater streams**
  - **Empirical data not solely theoretical data**

Approximation of Typical Heavy Metal Mass Balance

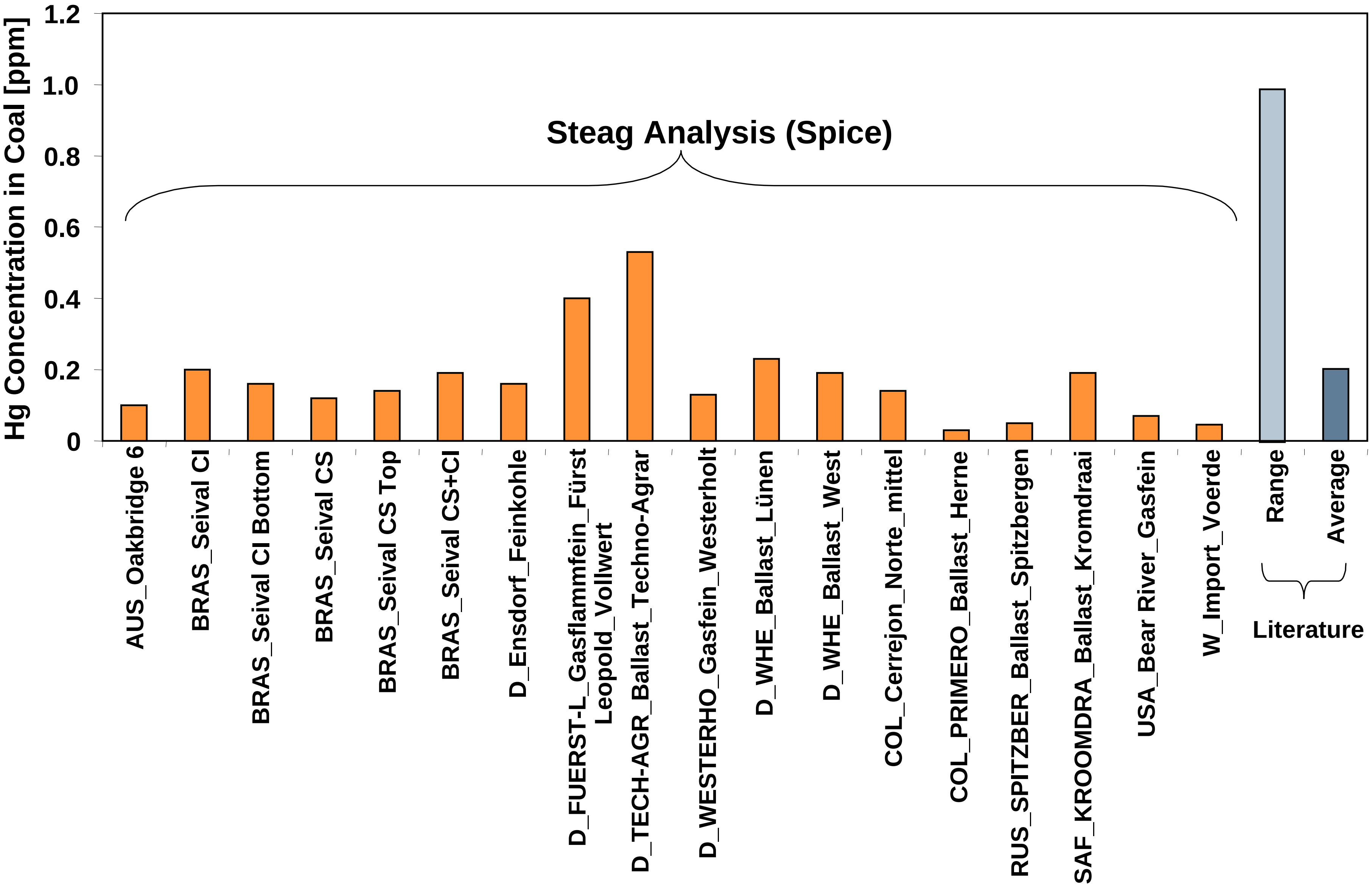


Ash:
97 % HM 1
68 % HM 2
5 % HM 3

Gypsum slurry:
2.7 % HM 1
30 % HM 2
85 % HM 3

HM 1 = As, Ag, Ba, Be, B, Cd, etc.
HM 2 = Se
HM 3 = Hg

Typical Hg Concentrations in Coal



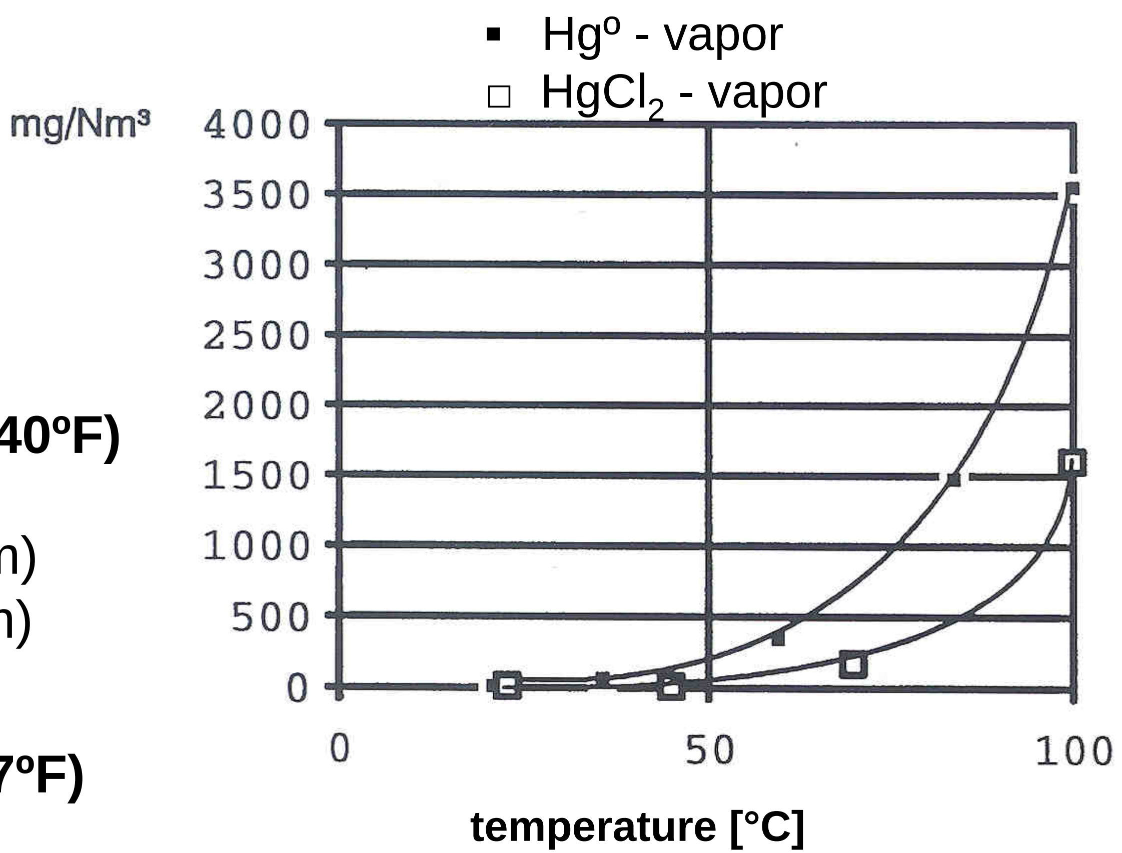
Chemical and Physical Properties of Hg and Hg Compounds

Boiling Point

Hg^0	357°C (675ºF)
$HgCl_2$	302°C (576ºF)
Hg_2Cl_2	384°C (723ºF)

Vapor Pressure (at 60°C, 140ºF)

Hg^0	320 mg/m³ (36 ppm)
$HgCl_2$	130 mg/m³ (11 ppm)



Solubility in Water (25°C, 77ºF)

Hg^0	3×10^{-6} g/l	→	low water solubility
$HgCl_2$	72 g/l	→	high water solubility

Relevant Reactions of Hg with Cl

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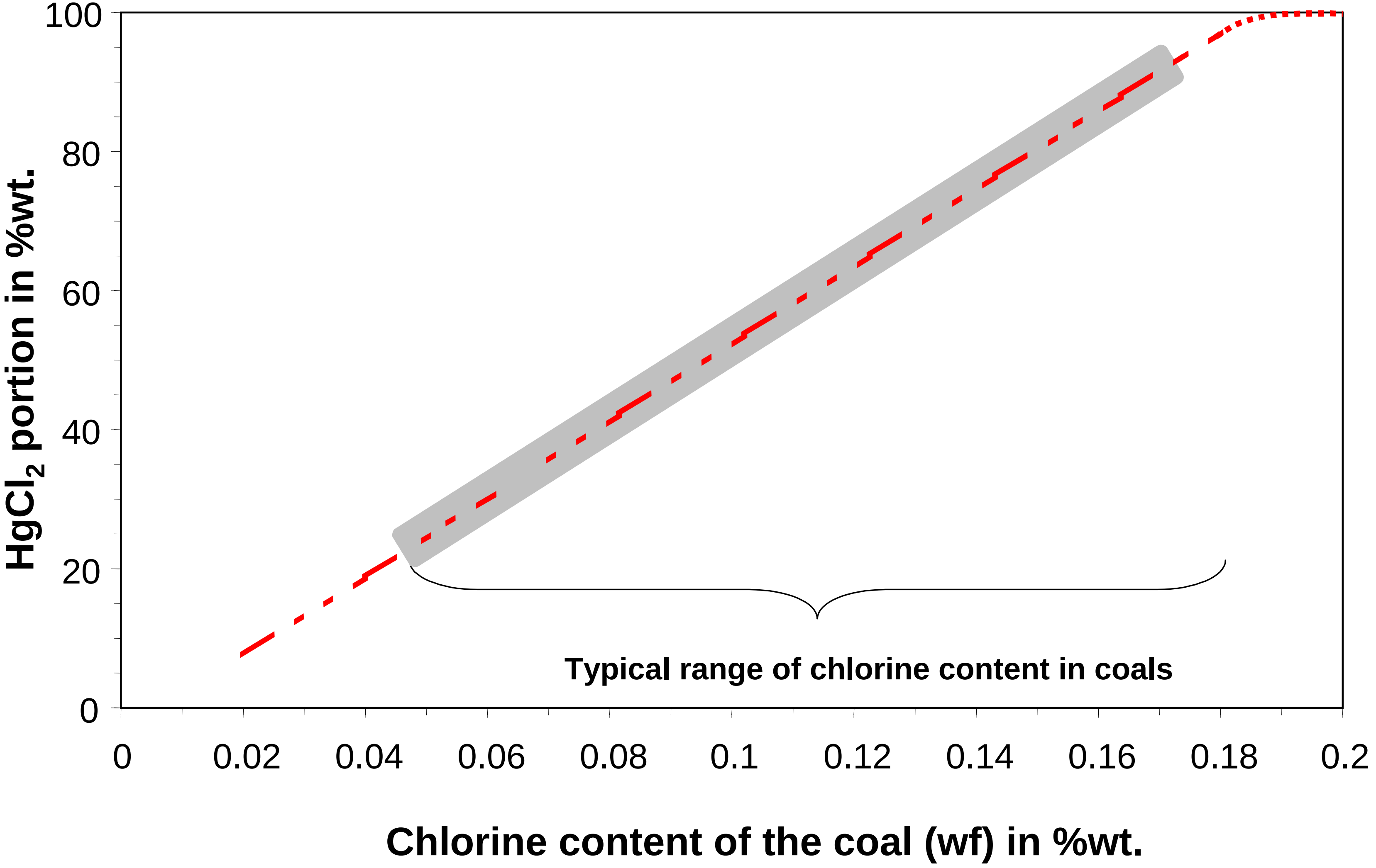
Formation of Mercury Oxide in the Furnace	$2\,Hg + O_2 \rightleftharpoons 2\,HgO$
Formation of Elemental Chlorine in the Furnace	$4\,HCl + O_2 \rightleftharpoons 2\,H_2O + 2\,Cl_2$
Oxidation of Mercury	$Hg + Cl_2 \rightleftharpoons HgCl_2$
Consumption of Cl_2 by SO_2	$SO_2 + Cl_2 + H_2O \rightleftharpoons SO_3 + 2HCl$
Reduction of Mercury Oxide	$HgO + SO_2 \rightleftharpoons Hg + SO_3$

- **These reactions are important for the oxidation of elemental mercury in the furnace and boiler, the generation of Cl_2 and subsequent formation of ionic mercury.**
- **The reduction of ionic mercury and the consumption of Cl_2 by SO_2 could be seen as the most important reactions in the area of the furnace and boiler determining the speciation between Hg^0 and Hg^{2+} in case of high SO_2 concentrations.**

Influence of the Cl-Content of Coal on the $HgCl_2$ Portion

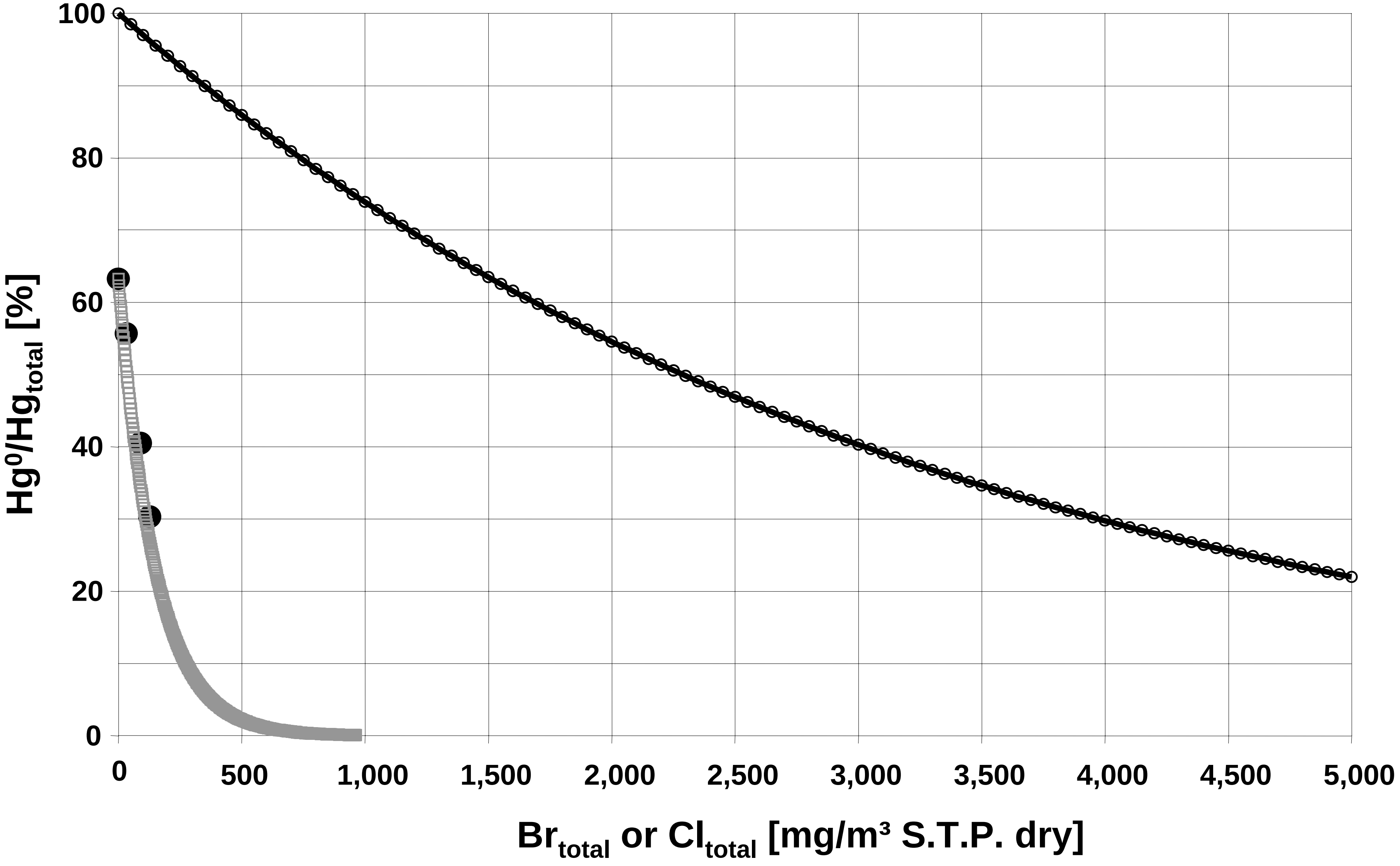


Relevant Reactions of Hg with Br

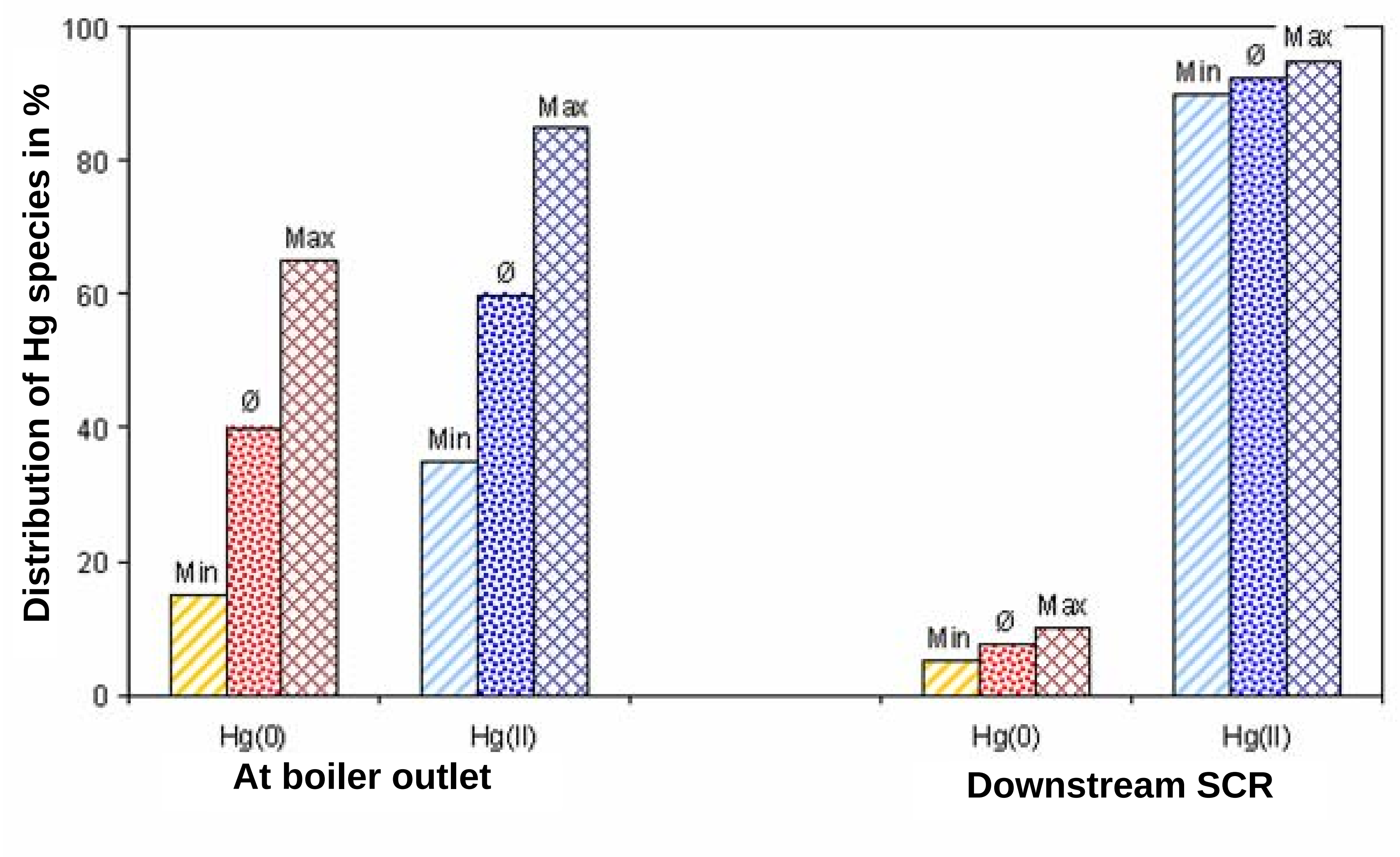
Formation of Mercury Oxide in the Furnace	$2\,Hg + O_2 \rightleftarrows 2\,HgO$
Formation of Elemental Bromine in the Furnace	$4\,HBr + O_2 \rightleftarrows 2\,H_2O + 2\,Br_2$
Oxidation of Mercury	$Hg + Br_2 \leftrightarrows HgBr_2$
Consumption of Br_2 by SO_2	$SO_2 + Br_2 + H_2O \rightleftarrows SO_3 + 2HBr$
Reduction of Mercury Oxide	$HgO + SO_2 \rightleftarrows Hg + SO_3$

⇨ The difference between the effectiveness of Br_2 in oxidizing Hg^0 compared to Cl_2 in oxidizing Hg^0 results from the fact that Cl_2 is consumed faster than it is generated, particularly in the case of high SO_2 concentrations. The Cl_2 consumption reaction is thermodynamically favored while the Br_2 consumption reaction is thermodynamically not favored, since its reaction enthalpy is strongly positive over the whole temperature range of the boiler (Vosteen et. al).

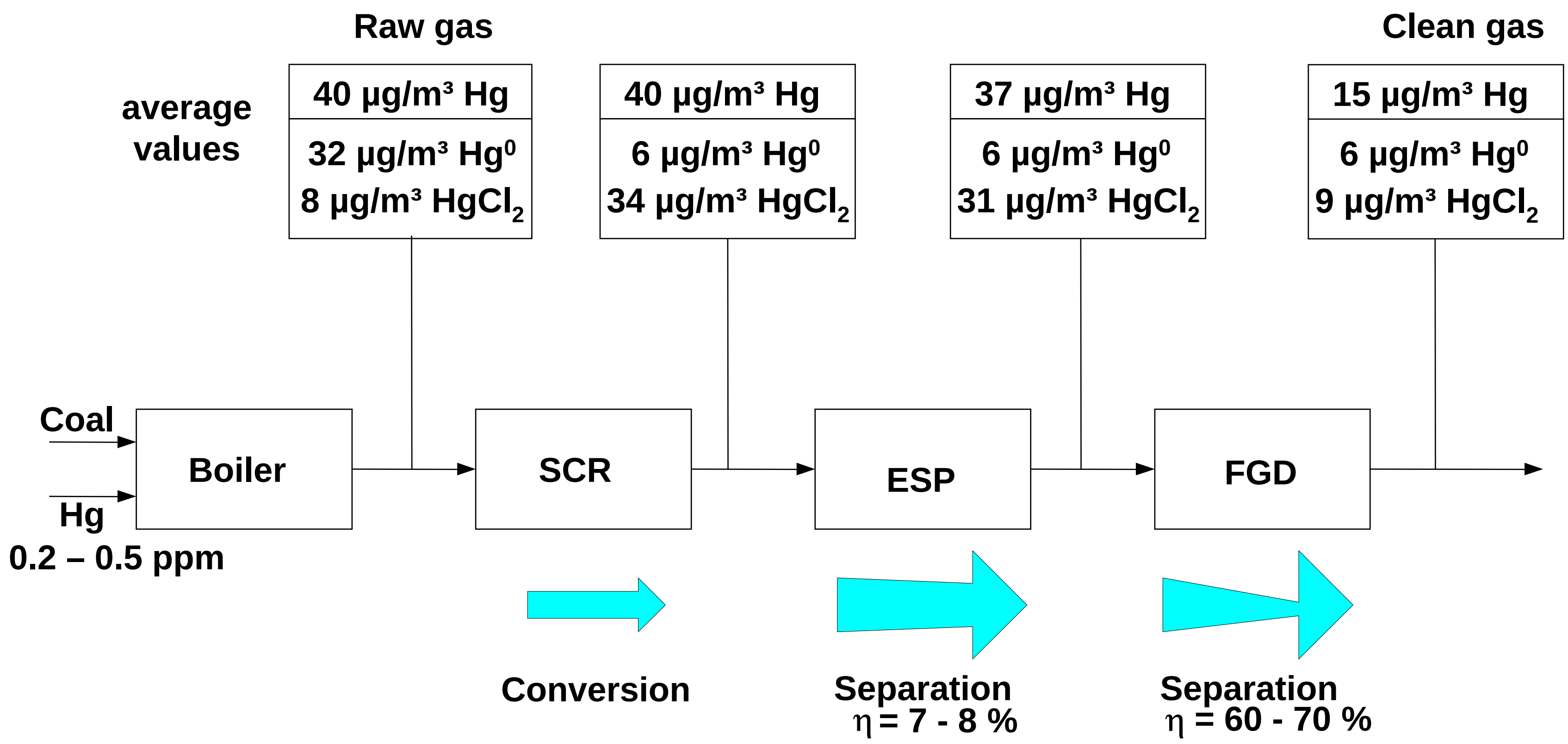
Hg Oxidation Potency of Cl and Br



Influence of SCR on Hg Speciation Upstream of FGD

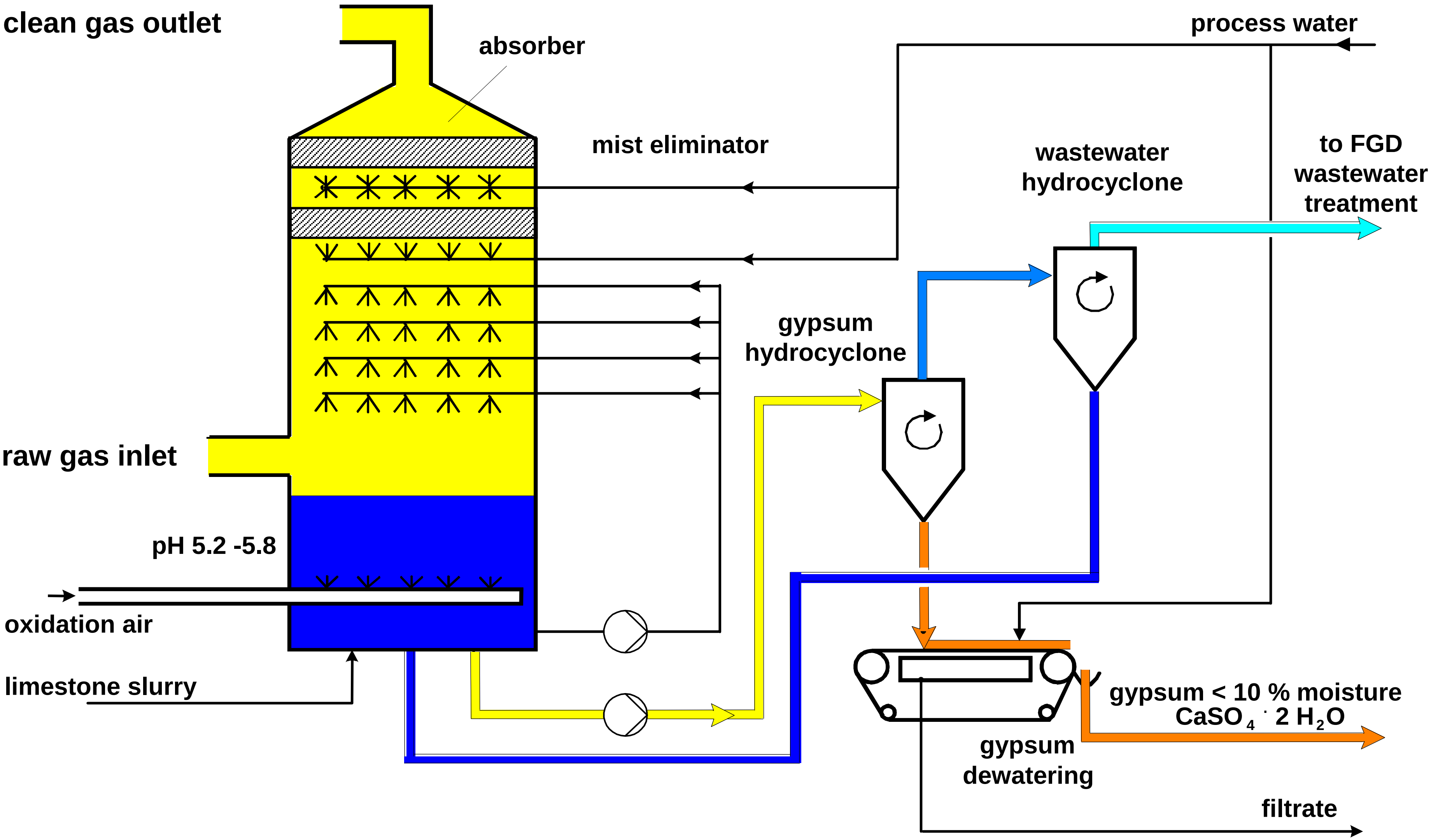


Hg Balance of Steag's Voerde Units 3 and 4



Bituminous coal:	**Heating value**	**11,200 – 11,700 Btu/lb**
	H_2O	**6 - 11 %wt.**
	Ash	**6 - 12 %wt.**
	Chlorine	**0.035 %wt.**
	Fluoride	**0.006 %wt.**
	Sulfur	**0.6 – 1.0 %wt.**

Typical Modern Wet Limestone Forced Oxidation FGD Process



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Typical FGD Wastewater Composition Before and After Treatment

Compound	FGD Wastewater [ppm] before treatment	FGD Wastewater [ppm] after treatment
solids	8,000 - 15,000	< 30
chloride	5,000 - 40,000	5,000 - 40,000
sulfate	1,500 - 2,500	1,000 - 1,800
sulfite	< 20	< 20
fluoride	< 50	< 30
copper	< 5	< 0.5
zinc	< 10	< 1.0
nickel	< 5	< 0.5
chromium	< 5	< 0.5
cadmium	< 1	< 0.05
mercury	< 1	< 0.05
lead	< 5	< 0.1
sulfide	< 20	< 0.2
nitrate	10 - 2,000	10 - 2,000
nitrite	< 2	< 2
ammonia/ammonium	< 10 - 100	< 10 - 100

Optimized FGD Wastewater Treatment Process

Conventional FGD Wastewater Treatment Process:

- Conventional treatment of FGD wastewater in a one-stage process with external disposal of 100% of the sludge residue produced
- Disadvantage:
  - High disposal costs for the sludge

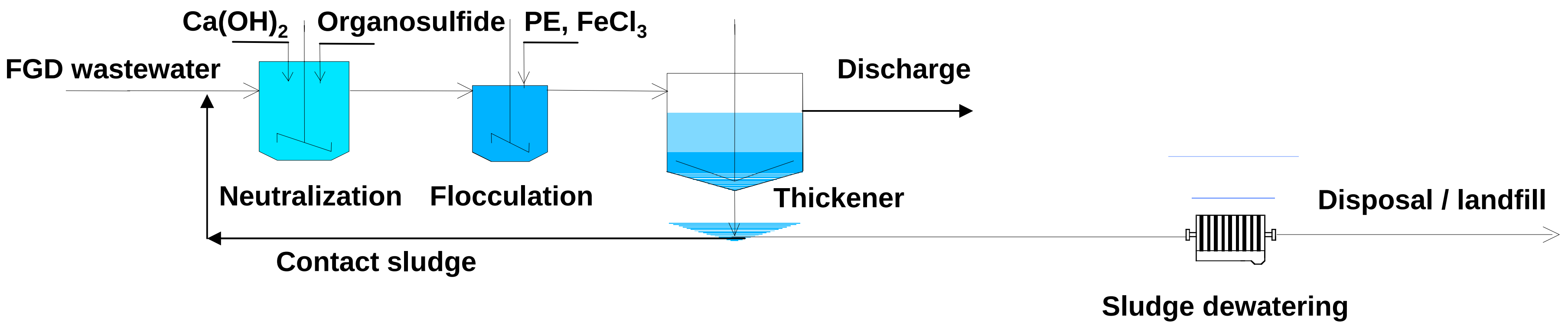
Steag's Patented FGD Wastewater Treatment Process:

- Selective Hg removal using a two-stage FGD wastewater treatment process with internal recycling of >95% of the sludge residue produced
- Minimized amount for external disposal
- Separation of the sludge in two fractions:
  - 95 – 98 % with a very low heavy metal content, particularly Hg
  - 2 – 5% with a very high heavy metal content, particularly Hg

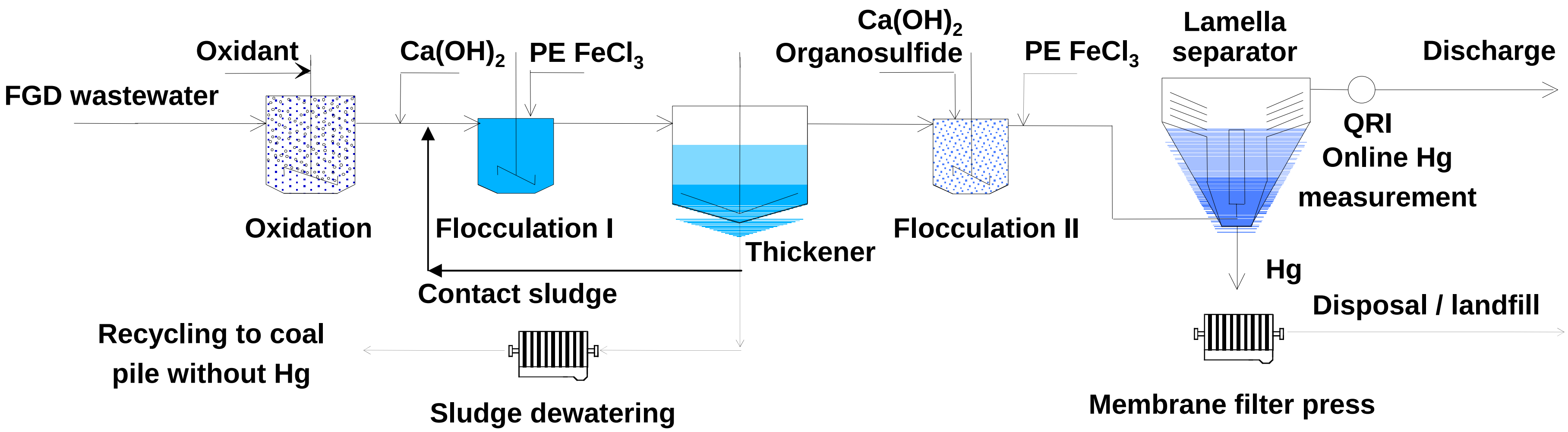
Advantage:

  - > 95% reduction of the sludge disposal costs

Conventional One-stage Process



Steag's Two-stage Process with Selective Hg Separation



Selective Hg Separation from FGD Wastewater at Steag's Herne Cogeneration Plant

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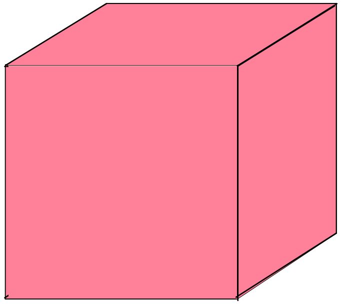
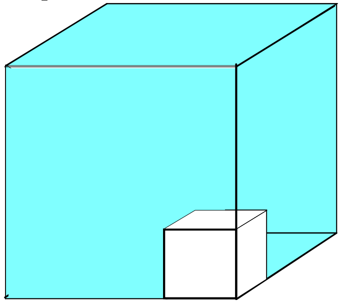
Until 2000: 6,500 t/a of WWT filter cake to disposal



Composition: gypsum, lime, inert silicate and other fly ash constituents, heavy metals including Hg

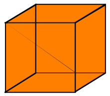
97 % | **3 %**

Since 2000:
6,300 t/a of heavy metal free WWT filter cake recycled back to the coal pile



Composition: gypsum, lime, inert silicate and other fly ash constituents

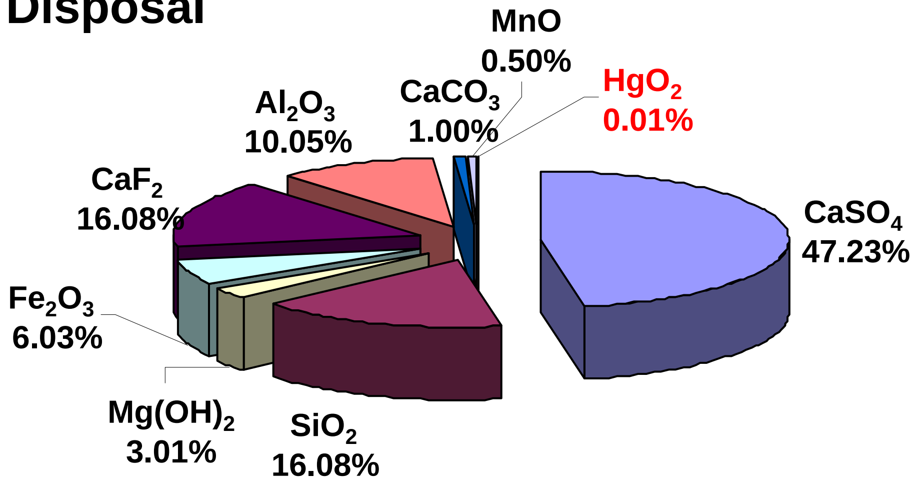
Since 2000:
200 t/a of heavy metal WWT filter cake to a disposal landfill



Composition: gypsum, lime, inert silicate and other fly ash constituents, heavy metals including Hg

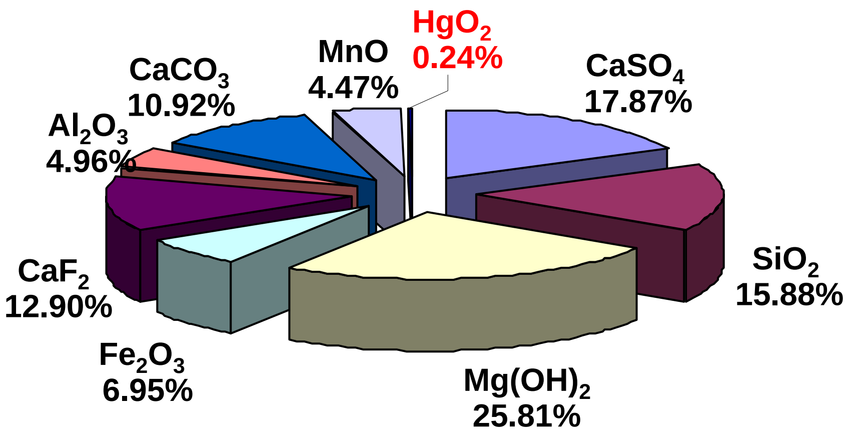
Filter Cake Composition Before 2000

Filter Cake To Disposal

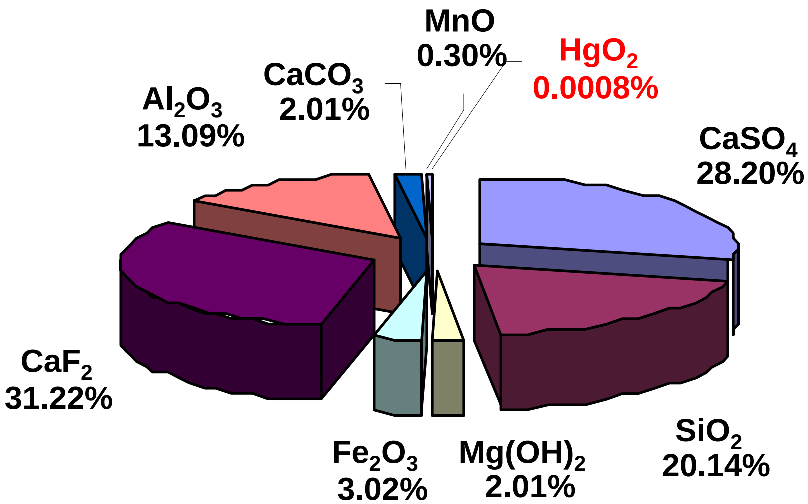


Filter Cake Composition Since 2000

Filter Cake To Disposal



Filter Cake Back To Coal Pile



Optimized FGD Wastewater Treatment Process

Actual situation until 2000 with the conventional single-stage WWTP

- Filter cake amount to disposal: 6,500 t/a
- Specific disposal cost: 90 €/t
- Total FGD WWT operating costs: 585,000 €/a

After retrofit of the two-stage WWTP and recycling of heavy metal free filter cake back to the coal pile:

- Filter cake amount back to the coal pile: 6,300 t/a
- Filter cake amount to deposit 200 t/a
- Specific disposal cost: 150 €/t
- Total Disposal costs: 30,000 €/a
- Additional chemical consumption cost: 50,000 €/a
- Total FGD WWT operating cost: 80,000 €/a

Total saving of FGD WWT operating cost: 505,000 €/a

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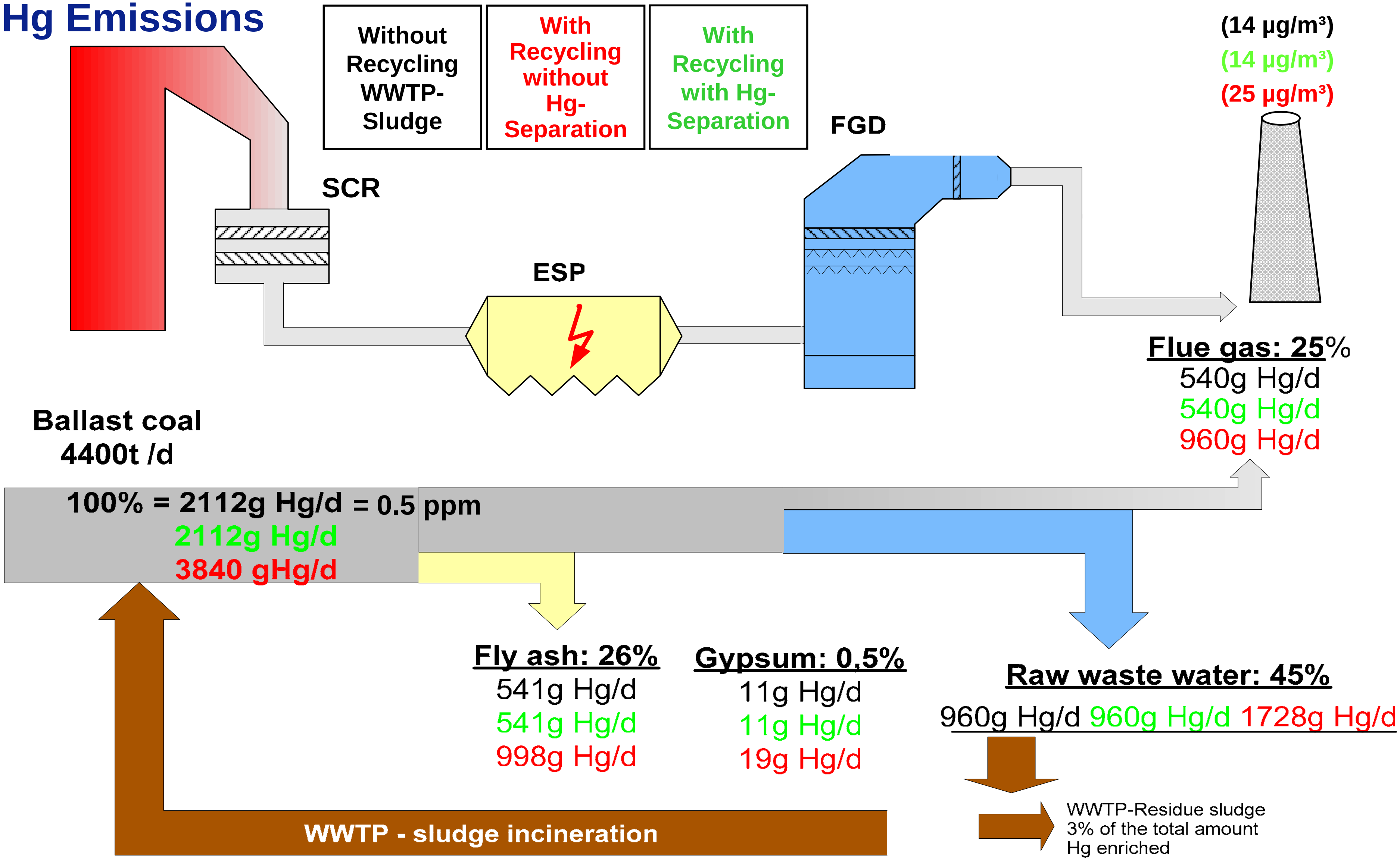
Influence of Internal FGD WWT Sludge Recycling and on Hg Emissions



?? Questions ??