Mercury-Related Chemistry in Waste Incineration and Thermal Process Flue Gases Bernhard W. Vosteen, Vosteen Consulting GmbH, Cologne (Germany) Richard Ullrich, WastePro Engineering...

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Bernhard W. Vosteen, Vosteen Consulting GmbH, Cologne (Germany)
Richard Ullrich, WastePro Engineering Inc., Kenneth Square, PA

Chlorine Enhanced Hg-Oxidation

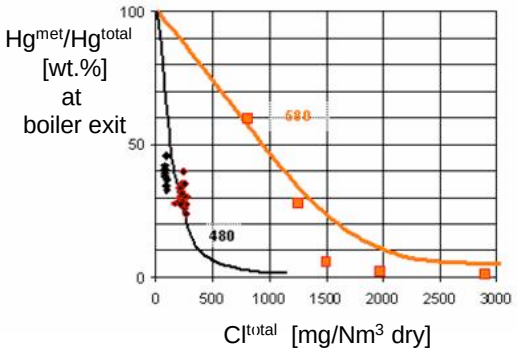
Main global reactions		individual Stoptemperatures
$4\ HCl + O_2 \leftrightarrow 2\ H_2O + 2\ Cl_2$	Chlorine-Deacon-Reaction	680 °C
$SO_2 + Cl_2 + H_2O \leftrightarrow SO_3 + 2\ HCl$	Chlorine-Griffin-Reaction	< 380 °C (boiler exit)
$SO_2 + ½\ O_2 \leftrightarrow SO_3$	SO_2/SO_3-Konversion	900 °C
$Hg + Cl_2 \leftrightarrow HgCl_2$	direct Hg-Chlorination*)	580 °C …… 480 °C

*) $Hg + 2\ HCl + ½\ O_2 \leftrightarrow HgCl_2 + H_2O$ *indirect Hg-Chlorination in boiler not relevant, but in SCR (V_2O_5 as oxigen donator)*

Plant test run evaluation results and model curves for Hg^{met}/Hg^{total} at boiler exit

Combustion of hazardous wastes
11 vol.% O_2 dry,
8 vol.% H_2O

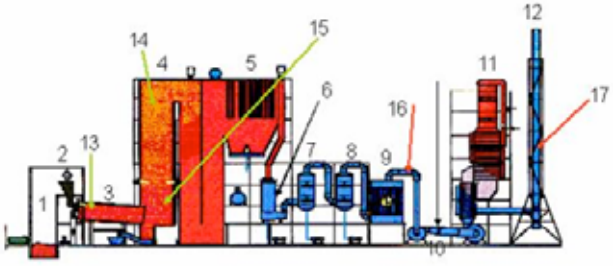
Stoptemperature of direct Hg-chlorination: 580°C



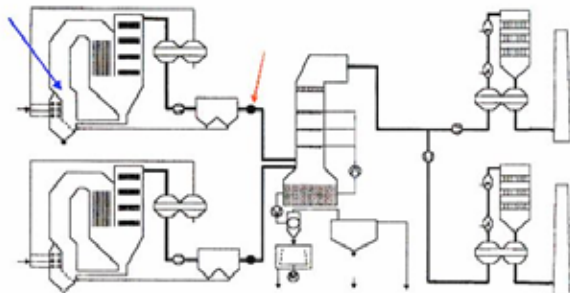
Combustion of coal and sewage sludge
5 vol.% O_2 dry,
3.6 vol.% H_2O

Stoptemperature of direct Hg-chlorination: 480°C

Hazardous waste incinerator



Industrial power station (100 MW_{therm})



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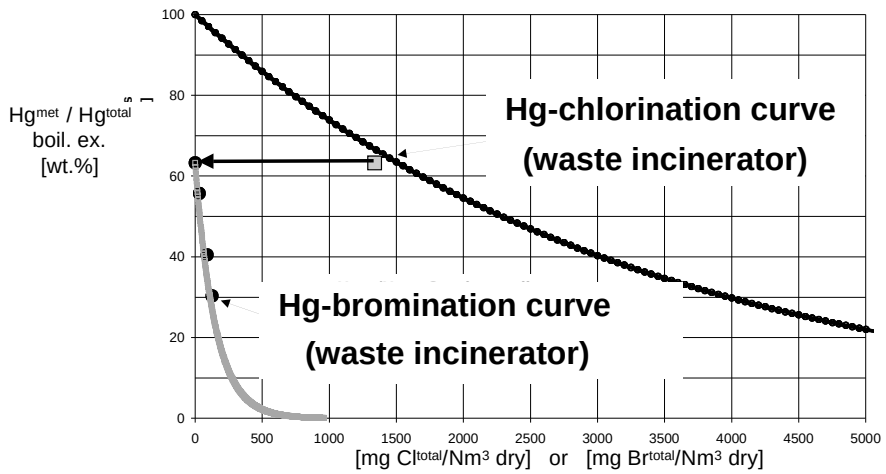
Bromine Enhanced Hg-Oxidation

Main global reactions	(hypothesis Vosteen)	Thermodynamics in boiler temperature range
$4\ HBr + O_2 \leftrightarrow 2\ H_2O + 2\ Br_2$	Bromine-Deacon-Reaction	$\Delta_R G < 0$
$SO_2 + Br_2 + H_2O \leftrightarrow SO_3 + 2\ HBr$	Bromine-Griffin-Reaction	$\Delta_R G >> 0$
$SO_2 + ½\ O_2 \leftrightarrow SO_3$	SO_2/SO_3-Konversion	$\Delta_R G < 0$
$Hg + Br_2 \leftrightarrow HgBr_2$	direct Hg-Bromination*)	$\Delta_R G < 0$
$SO_2 + Br_2 \leftrightarrow SO_2Br_2$	Bromine-Sulfurylisation	$\Delta_R G << 0$
$Hg + SO_2Br_2 \leftrightarrow HgBr_2 + SO_2$	Hg-Bromination by SO_2Br_2	$\Delta_R G < 0$

*) $Hg + 2\ HBr + ½\ O_2 \leftrightarrow HgBr_2 + H_2O$ *indirect Hg-Bromination in boiler not relevant, but in SCR (V_2O_5 as oxigen donator)*

Bromine > 25 times more effective for Hg^{met} oxidation than chlorine in waste incineration as well as in coal combustion

(BAYER patent applications pending world wide)



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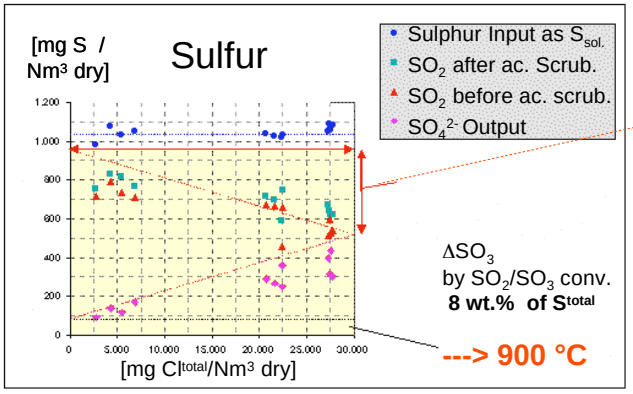
A) Closed Sulfur and Chlorine Balances

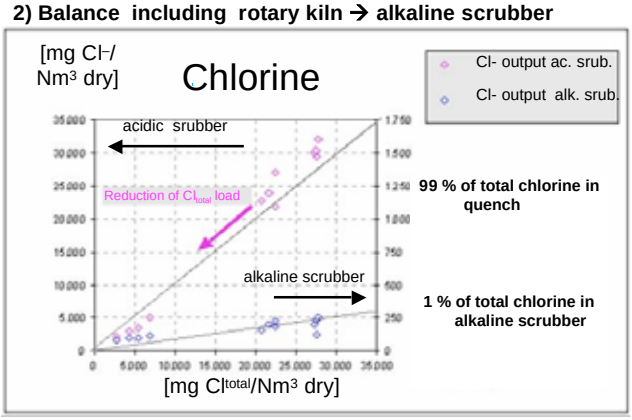
1) Balance including rotary kiln → acid srubber



ΔS = 400 mg S/Nm³ dry
= 12.5 mmol S/Nm³ dry
ΔCl_2 = 12.5 mmol Cl_2/Nm³ dry
= 886 mg Cl_2/Nm³ dry

3 wt. % Cl_2 of Cl^{total}
(Cl_2 resuppression in boiler via Griffin reaction)

2) Balance including rotary kiln → alkaline scrubber

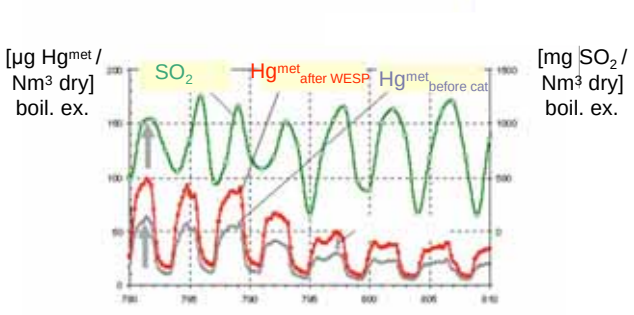


Total intermediate Cl_2 in boiler flue gas: 4 wt. % of Cl^{total}

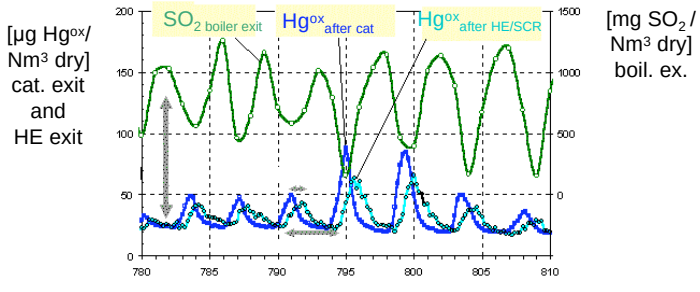
1 wt. % Cl_2 of Cl^{total}
(Cl_2 absorption in alkaline scrubber)

--- > 680 °C for Cl-Deacon
< 380 °C for Cl-Griffin (running until boiler exit)

B) Periodically oscillating SO_2 raw gas load



Cl_2 resuppression by SO_2 in boiler -- > less Hg^{ox} at boiler exit
--- > cocurrent Hg^{met} at boiler exit



less residual SO_2 -- > less Cl_2 in SCR -- > less Hg-oxidation in SCR
--- > countercurrent Hg^{ox} behind Tail-End-SCR

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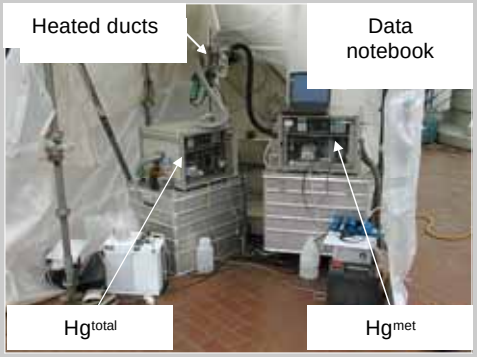
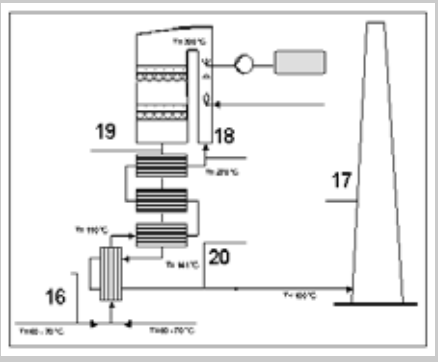
Simulated Hg-loads (continuous and discontinuous mercury feeding)

Continuous Monitoring of Hg^{total}- and of Hg^{ox}

with 4 or 2 x 2 monitors in parallel (*HM1400 of DURAG/Verewa*)





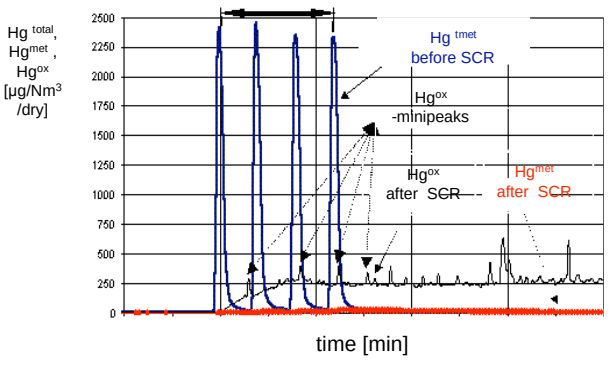
2 external and 2 internal measuring points at Tail-End- SCR

Hg^{met}-Adsorption in SCR

before SCR Hg^{met} only

Hg-bottles (1 x 26 g Hg)

after SCR Hg^{ox} only, no Hg^{met}



Hg^{ox} -Desorption promoted by HCl/Cl_2