The Influence of Fuel Chlorine & Bromine on Dioxins and Furans at Waste Incinerators and Coal-Fired Power Plants – as related to Bromine Enhanced Mercury Abatement

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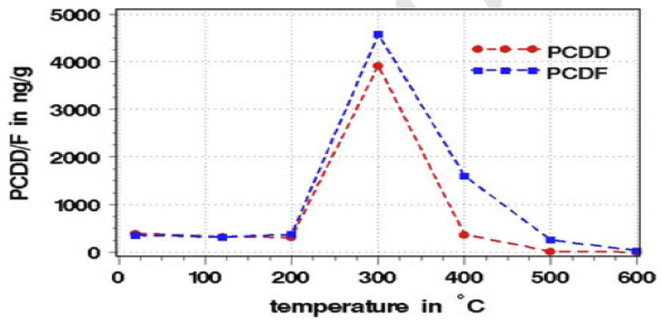
PCDD/F in Waste Incineration

• Polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF) are mainly formed by de-novo synthesis primarily in the boiler back end section (at the post-superheater temperature range 500 - 200 °C). Vogg and Stieglitz 1987, Funcke 1993, 2001, Vehlow 2012.

• PCDD/F de-novo synthesis appears to be a quite slow reaction that predominantly proceeds as oxy-chlorination of residual carbon or soot particles in the boiler ash deposits, where inorganic chlorides are the local chlorine source with e.g. $CuCl_2$ acting as catalyst. Hagenmaier 1989, Hunsinger 2006.

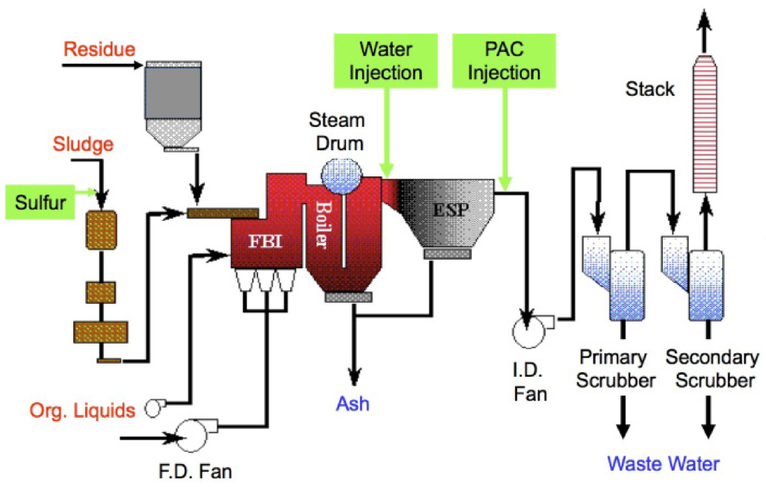


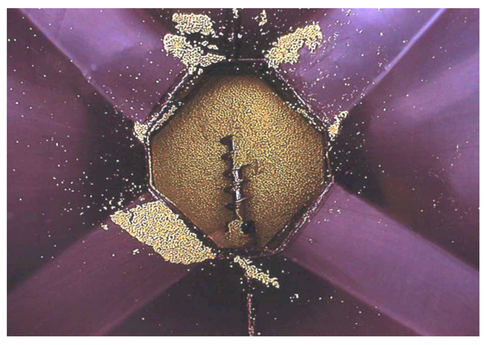
Formation of PCDD/F in waste incineration fly ashes hetaed in air atmosphere.

Vehlow 2012 (adopted from Stieglitz and Vogg 1987)

• But, increased halogen inventories in the fuels have no marked influence on the PCDD/F concentration in the incinerator raw gas. Vehlow 1996, Funcke 1995, 1998, see also Kerber 1994, Rigo 1995.

• Tests at a commercial stationary Fluidized Bed Incinerator firing chlorine-rich residues and industrial sludges demonstrated that sulphur addition inhibits the formation of PCDD/F considerably. Vosteen 2001a, 2001b. See also Lindbauer 1992, Gullet 1992, 1996, Luthe 1998, Xie 2000.





Sulfur granulat bin with screw conveyor for granulat dosage. Vosteen 2001a

Dioxin Tests March 2000

• 5 test conditions (3 runs each) were carried out

Test Run #	1	2	3	4	5
PAC (lb/hr)		19	19	18	19
Sulfur (lb/hr)				15	15
Fbd (°C)	1000	976	932	932	983
ESP (°C)	162	163	188	195	175
PCDD/F (ng I-TEQ/Nm³@ 7% O_2) *	1.2	2.9	3.6	0.2	0.3

* Avg. of three datapoints

• Sulfur/PAC addition tests showed lowest Dioxin concentrations

Tests in March 2000 at a FBI (15,000 Nm³/h) of BAYER Polymers LLC. Vosteen 2001b

• Short-term fluctuations of the SO_2 level demonstrated no significant influence on the PCDD/F raw gas concentrations. This indicates that PCDD/F are not produced via gas-phase reactions or at fly ash particles during their flight through the boiler. Hunsinger 2006.

• However, a permanent increase of the SO_2 level as achieved by sulphur addition is inhibiting PCDD/F formation considerably, because high SO_2 concentrations in the boiler gas are causing sulfation of the metal chlorides (and metal bromides) - thus lowering halogenide concentrations in the ash deposits. Hunsinger 2006.

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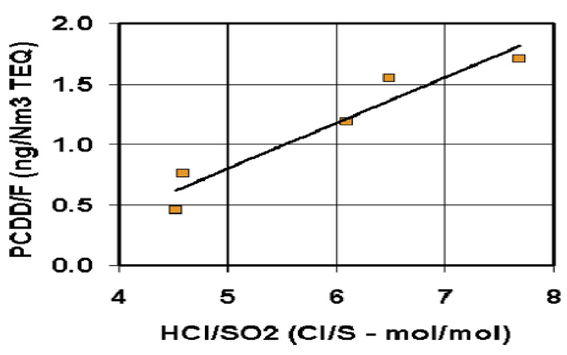
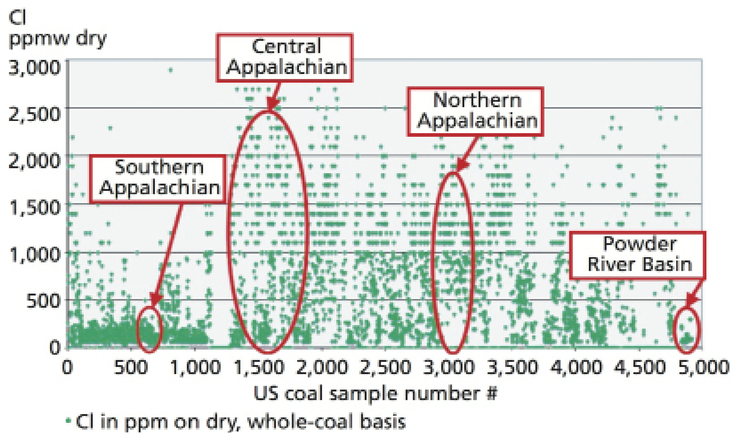


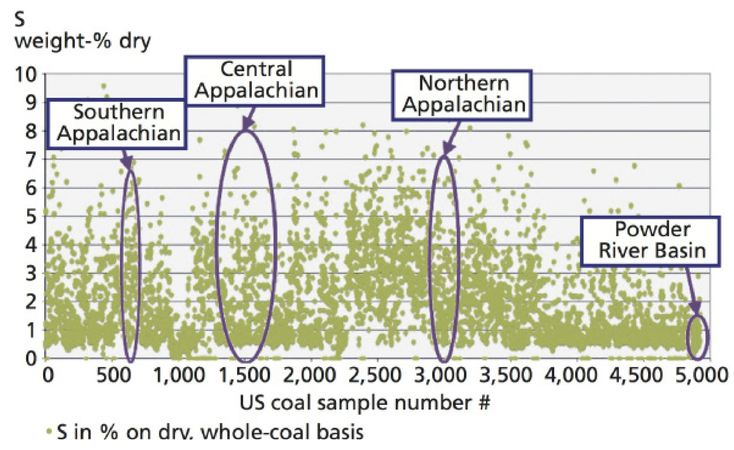
Reduced PCDD/F formation at low molar Cl/S ratios. Hunsinger 2006

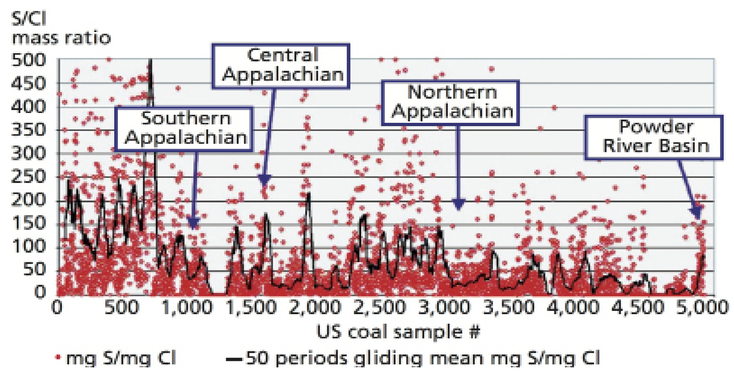
PCDD/F in Coal Combustion

• Main reasons for only little PCDD/F denovo synthesis in coal combustion are

- the high quality design of the combustion process with respect to controlled combustion and optimal burnout,
- stationary conditions (except of regular load changes)
- particulate scrubbers for fly ash separation (ESP, FF) working well below 200 °C,
- the native chlorine contents in combination with comparatively high sulfur contents in the fired coals lead to high S/Cl mass ratios (see graphs below) - except at coal-fired CFBs with primary desulfurization by limestone/lime addition into the fluidized bed.







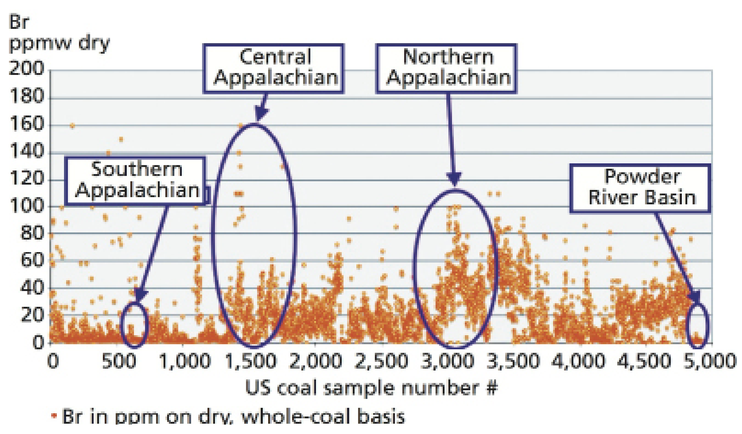
Chlorine and Sulfur in 5000 US coals (courtesy Prof. H. Belkin, USGS). Vosteen 2010

• Modern coal-fired boilers therefor yield very low PCDD/F concentrations in the boiler raw gas respectively at the stack. Mean stack emissions at PC-fired boilers are typically well below 0.01 ng I-TEQ/Nm³ (e.g. 0.003 ng I-TEQ/Nm³). Funcke 1997, 2012, Leckner 2007.

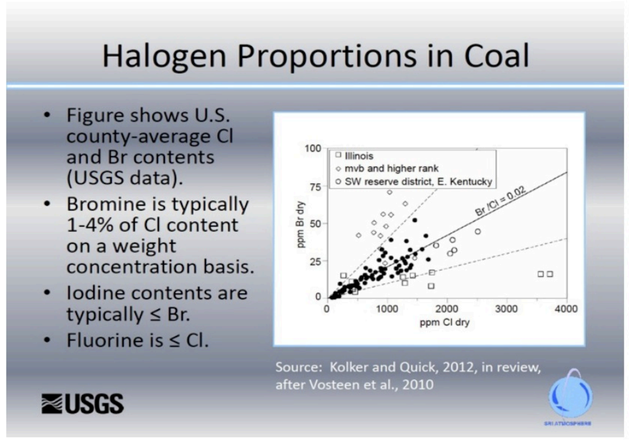
Native Bromine in Fossile Fuels

• Chlorine and bromine are present in all fossile fuels. The Br/Cl mass ratio in coal is normally about only 0.01 – 0.04 (in the mean 0.02). Vassilev 2000, Vosteen 2010, Vainikka 2012, Kolker 2012.

• The S/Br mass ratio is normally >> 250 (i.e. at least two orders of magnitude greater than the S/Cl mass ratio of the fired coals).



Bromine in 5000 US coals (courtesy Prof. H. Belkin, USGS). Vosteen 2010



Bromine versus Chlorine in US coals. Kolker 2012

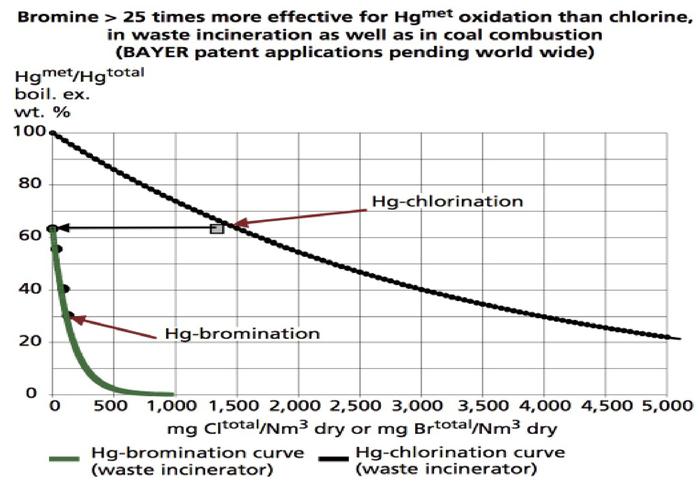
Bromide Addition to Waste or Coal

• Enhanced Mercury Oxidation is achieved by Pre-combustion Halogenide Addition to the fired fuels (Waste or/and Coal) – as succesfully demonstrated in commercial scale with BAYER / Currenta since 2001. Vosteen 2002.

• Addition of bromide is far more effective in mercury oxidation than that of chloride, because the high-temperature decomposition of bromide salts provides far more free halogenes. Vosteen 2002, 2003.

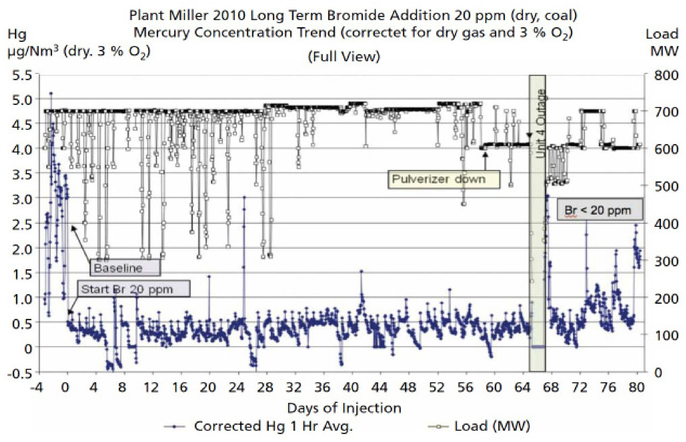
• Cl_2 is reduced by SO_2 back to HCl already at high temperatures (Chlorine Griffin Reaction), thus inhibiting mercury chlorination.

• However, Br_2 is reduced by SO_2 back to HBr only at low temperatures in the APC system (Bromine Griffin Reaction), but not yet at high temperatures, and is therefore available to oxidize elemental mercury forming mercury bromide all over the boiler temperature range – even in presence of SO_2. Kanefke 2008.



Mercury bromination more effective than mercury chlorination. Vosteen 2003

Sodium Bromide (NaBr) dosing pumps at stationary FBI for sewage sludge.



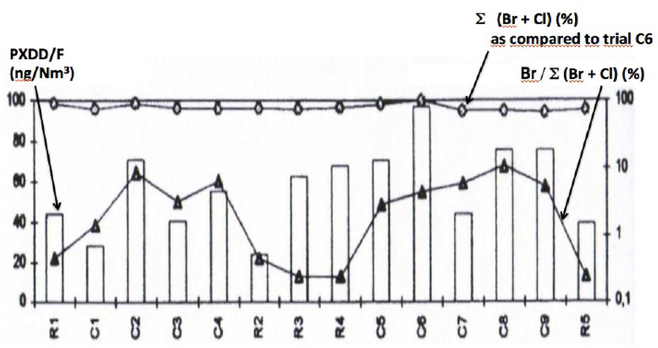
Calcium Bromide($CaBr_2$) at PC-fired Plant Miller (700 MWe). Berry 2011

PXDD/F

• An increase of the Br/Cl ratio in the fired waste (e.g. by co-combustion of electronic waste containing brominated flame redardants) correlates with an increase of PBCDD/F concentrations (mainly low brominated congeners). Funcke 1997, 2012.

• As observed in the flue gas of waste incinerators, the bromine containing congeners are formed **at the expense of the purely chlorinated PCDD/F**. The total concentration of all PXDD/F (X = halogen) is not influenced by varying Br/Cl ratios. Funcke 1997, 2012, Vehlow 2012.

• No tetra- to octabrominated congeners and also no tetra- to octabrominated polychlorinated cogeners will be detected when using a sampling period of 6 h according to DIN/ EN 1948.



PXDD/F raw gas concentrations of a test incinerator in relation to the total halogen input (trial C6 = 100 %) and to the molar Br portion (% of total Cl + Br) in 5 reference trials R1 - R5 and 9 co-combustion trials C1 - C9. Funcke 1997

• These findings (resulting from numerous co-combustion trials) are expected to be valid for coal-fired power plants - with and without pre-combustion bromide addition for enhanced mercury capture - , as well. Funcke 2012.

A list of references is available. Please ask authors.

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