Dioxins and Furans –

Reduction Measures in the Steel Industry

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Agenda

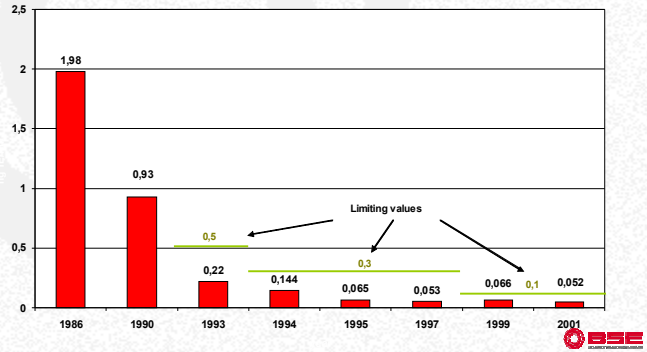
- Introduction
- Dioxins and Furans – properties and formation mechanisms
- Principles of dioxin and furan reduction
- Dioxin and Furan reduction in EAF plants
- Best Available Techniques Reference Document
- Conclusion

Badische Stahlwerke Kehl/Germany

- Founded 1968
- 1,97 Mio t good billets (2004)
- 2 EAFs (90 t)
- 2 rolling mills
- rebar/wire rod
- 750 employees

First Dioxin/Furan measurement in a steel plant in 1986

Stack emissions of PCDD/PCDF at BSW from 1986 to 2001



Dioxin and Furan – hazardous substances

- Known to European public since 1976 because of an industrial accident in Seveso, Italy.
- "By-product" of Agent Orange used in Vietnam by USA

PCDD/PCDF	are lipophilic, they therefore accumulate in mothermilk
	are affecting the immune system
	cause metabolic disorder
	cause liver disease
	are carcinogenic

Legislation in Europe regarding Dioxin/Furan

Origin of the limiting values are the waste incinerators:

Directive 2000/76/EC on incinerating of waste

0,1 ng TEQ / Nm^3

There are different limiting values for different kinds of industries and in different countries. But the future is 0,1 ng TEQ / Nm^3!

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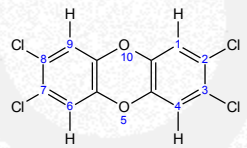
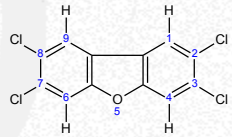
Dioxin and Furan - some chemistry



2,3,7,8-Tetrachlorodibenzo-(*p*)-dioxin



2,3,7,8-Tetrachlorodibenzo-furan

Dioxin and Furan - Toxicity equivalent factors

17 compounds with chlorine atoms in positions 2,3,7,8 are the most toxic

All these compounds have different toxicity

$$C_{PCDD/PCDF} = \sum_{i=1}^{17} f_i \cdot c_i$$

f_i : toxicity equivalent factor
c_i: concentration of individual compound

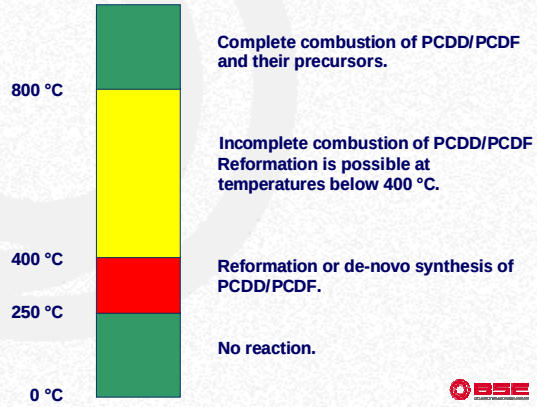
Dioxin and Furans – Physical Properties

- Dioxins and Furans are liquids with high boiling points.
- Dioxins and Furans tend to adsorb on dust particles.
- Above 100 °C Dioxins and Furans desorb from dust particles and can therefore pass the filter bags.

Dioxin and Furan - Formation Mechanisms

- Heterogeneous reaction of certain organic precursors (e.g. chlorophenols) on the surface of dust particles at a temperature around 250 - 400°C.
- *De-novo*-synthesis without organic precursors. Formation out of carbon, oxygen and metal chlorides at a temperature of about 300 °C.

Temperature Range for Dioxin Formation and Combustion



Dioxin and Furan Sources in the Steel Industry

Source	Time or place of formation	Emission factor
Electric arc furnace	Beginning of meltdown phase	0,07 – 9 µg TEQ / t of steel
Sinter plant	Upper region of sinter bed after ignition	1 – 10 µg TEQ / t of sinter
Foundry	Upper region of cupola furnace	0,03 – 10 µg TEQ / t of iron

Source: Standardized Toolkit for Identification and Quantification for Dioxin and Furan Releases UNEP Chemicals, Geneva, Switzerland, 2001

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Dioxin and Furan - Methods for Minimising Emissions

- **Primary measures**
  - Avoiding the formation of PCDD/PCDF in the system.
- **Secondary measures**
  - Decomposition or adsorption of PCDD/PCDF in the off-gas system.

Dioxin and Furan - Primary measures

- Selection of raw material (no oils, organic compounds, carbon and other material containing precursors for PCDD/PCDF formation).
- "Cleaning " of scrap (for EAF).

Significant PCDD/PCDF reduction with primary measures is difficult if not impossible.

Dioxin and Furan - Secondary measures

- Prevention of re-formation by rapidly cooling the off-gas in a water-spray chamber below the reaction temperature of 250 °C.
- Adsorption of PCDD/PCDF on activated carbon or lignite either in a packed bed or as an additive to the off-gas.
- Catalytic decomposition of PCDD/PCDF in a special filter device at the end of the off-gas system.

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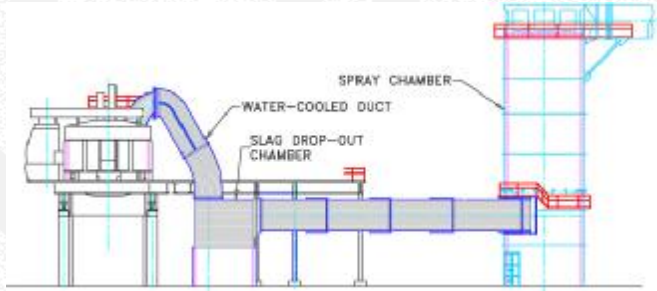
Dioxin and Furan Reduction in an EAF plant

- Post combustion. Burning off the PCDD/PCDF
- Quick cooling of the furnace exhaust to prevent re-formation of PCDD/PCDF
- Effective and reliable dust collection system at a suitable temperature.
- Lignite (activated carbon) injection for adsorption of PCDD/PCDF (complementary)

Quick Cooling by Injection of Water

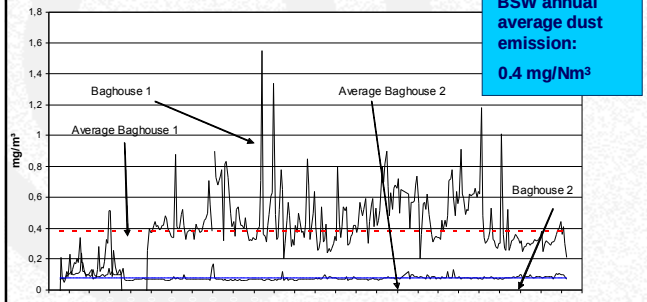


Controlling the Water Injection

- Modeling by CFD simulation
- Water amount is controlled by outlet temperature of the spraying chamber.
- All injected water is evaporated.

Mixing of primary and secondary fumes is necessary to dilute the moisture.

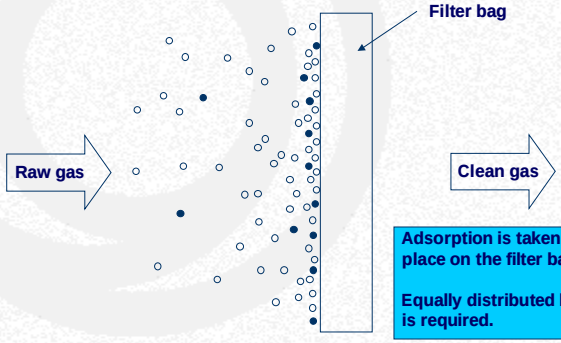
Effective and reliable dust collecting system with state of the art equipment



BSW annual average dust emission:

0.4 mg/Nm³

Principle of lignite injection

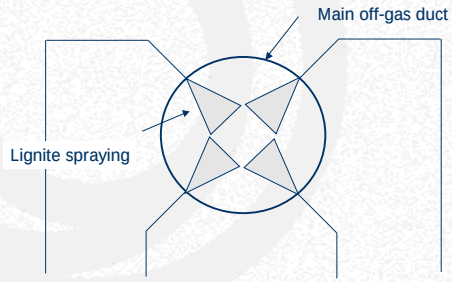


Adsorption is taken place on the filter bags.

Equally distributed lignite is required.

○ Dust particle ● Lignite particle

Way of Lignite Injection – equal distribution



- 20 - 40 kg/h of lignite
- 800 - 1000 Nm³/h carrier air
- place of adsorption are the filter bags

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BREF document describes already used methods seen to be best practice for a certain issue.

- Recommendation for sinter plants:

Primary measures	Recirculation of off-gas, raw material selection.
Secondary measures	Fabric filter and carbon injection or fine wet scrubbing

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- Recommendation for Foundries:

Primary measures	Raw material selection, circulation of off-gas.
Secondary measures	Post combustion, quenching, fabric filter and carbon injection (if necessary).

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Guiding principle for dioxin and furan reduction is always the same for all .

- Generation of high temperatures (> 600 °C) to destroy dioxins and furans.
- Quick cooling off-gas cooling to avoid re-formation of dioxins and furans.
- Reliable and efficient dust collection system at low temperatures (< 100 °C) to keep adsorbed dioxins and furans in the dust collector.
- Injection of carbon to improve adsorption rate on the dust.