EAF Environmental Impact:
Air Pollution

Karima Gandt, Dr.-Ing. Thomas Echterhof

VALEAF Seminar 3 „Energy Efficiency and Environment“
Milan, 09.04.2015
What do we mean by 'Air Pollution'?

PCDD, PCDF, VOC, PAH, PCB
NO\textsubscript{X}, SO\textsubscript{2}

Research driven by
• Health and environment, because organic pollutants are highly carcinogenic.
  → strict regulations especially for PCDD/F
• missing basic data (NO\textsubscript{X} and SO\textsubscript{2})

<table>
<thead>
<tr>
<th>Air emissions</th>
<th>Million Nm\textsuperscript{3}/h</th>
<th>1 – 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Off-gas flow</td>
<td>Nm\textsuperscript{3}/t LS</td>
<td>8000 – 10000</td>
</tr>
<tr>
<td>Dust</td>
<td>g/t LS</td>
<td>4 – 300</td>
</tr>
<tr>
<td>Hg</td>
<td>mg/m\textsuperscript{3}</td>
<td>0.35 – 52</td>
</tr>
<tr>
<td>Pb</td>
<td>mg/t LS</td>
<td>75 – 2850</td>
</tr>
<tr>
<td>Cr</td>
<td>mg/t LS</td>
<td>12 – 2800</td>
</tr>
<tr>
<td>Ni</td>
<td>mg/t LS</td>
<td>3 – 2000</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/t LS</td>
<td>200 – 24000</td>
</tr>
<tr>
<td>Cd</td>
<td>mg/t LS</td>
<td>1 – 148</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/t LS</td>
<td>11 – 510</td>
</tr>
<tr>
<td>HF</td>
<td>mg/t LS</td>
<td>0.04 – 15000</td>
</tr>
<tr>
<td>HCl</td>
<td>mg/t LS</td>
<td>800 – 35250</td>
</tr>
<tr>
<td>SO\textsubscript{2}</td>
<td>g/t LS</td>
<td>5 – 210</td>
</tr>
<tr>
<td>NO\textsubscript{X}</td>
<td>g/t LS</td>
<td>13 – 460</td>
</tr>
<tr>
<td>CO</td>
<td>g/t LS</td>
<td>50 – 4500</td>
</tr>
<tr>
<td>CO\textsubscript{2}</td>
<td>kg/t LS</td>
<td>72 – 180</td>
</tr>
<tr>
<td>TOC</td>
<td>g C/t LS</td>
<td>35 – 260</td>
</tr>
<tr>
<td>Benzene</td>
<td>mg/t LS</td>
<td>30 – 4400</td>
</tr>
<tr>
<td>Chlorobenzenes</td>
<td>mg/t LS</td>
<td>0.2 – 12</td>
</tr>
<tr>
<td>PAH (\textsuperscript{1})</td>
<td>mg/t LS</td>
<td>9 – 970</td>
</tr>
<tr>
<td>PCB (\textsuperscript{2})</td>
<td>mg/t LS</td>
<td>0.01 – 5</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>\mu g I-TEQ/t LS</td>
<td>0.04 – 6</td>
</tr>
</tbody>
</table>

Output data for EAFs within the EU before abatement [from BAT, 2013, 25521] \textsuperscript{4,5} means no consistent database
### Selected projects about air pollution

<table>
<thead>
<tr>
<th>Description</th>
<th>Report No.</th>
<th>Consortium</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimisation of environment and related energy utilisation in scrap-based steelmaking (Phase II)</td>
<td>18556</td>
<td>Dansteel Engineering</td>
<td>1993 - 1996</td>
</tr>
<tr>
<td>Effects of operational factors on the formation of toxic organic micropollutants in EAF steelmaking</td>
<td>21432</td>
<td>Corus UK, CSM, BFI, ISQ</td>
<td>2000 - 2003</td>
</tr>
<tr>
<td>Emissions reduction through analysis, modelling and control – ERAMAC</td>
<td>23333</td>
<td>TATA, CRM, GERDAU, ISQ, LECES, MEFOS, BFI</td>
<td>2003 - 2006</td>
</tr>
<tr>
<td>Development of catalytic metal filters for simultaneous removal of organic compounds and particulate matter from EAF fumes – CATIA</td>
<td>23737</td>
<td>LECES, Fraunhofer, LME, TNO</td>
<td>2003 - 2007</td>
</tr>
<tr>
<td>Control of nitrogen oxide emission at the electric arc furnace – CONOX</td>
<td>25078</td>
<td>RWTH-IOB, CSM, DEW, ORI, RIVA</td>
<td>2006 - 2009</td>
</tr>
</tbody>
</table>
### Organic air pollutants

<table>
<thead>
<tr>
<th>Selected projects</th>
<th>Report No.</th>
<th>Pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optimization of environment and related energy utilization in scrap-based steelmaking (Phase I)</td>
<td>16662</td>
<td>PCDD/F</td>
</tr>
<tr>
<td>Optimisation of environment and related energy utilisation in scrap-based steelmaking (Phase II)</td>
<td>18556</td>
<td>PCDD/F</td>
</tr>
<tr>
<td>Effects of operational factors on the formation of toxic organic micropollutants in EAF steelmaking</td>
<td>21432</td>
<td>PCDD/F, VOC, PAH, PCB</td>
</tr>
<tr>
<td>Emissions reduction through analysis, modelling and control – ERAMAC</td>
<td>23333</td>
<td>VOC, PAH, PCB NO\textsubscript{x}, SO\textsubscript{2}</td>
</tr>
<tr>
<td>Development of catalytic metal filters for simultaneous removal of organic compounds and particulate matter from EAF fumes – CATIA</td>
<td>23737</td>
<td>PCDD/F, VOC, PAH, PCB</td>
</tr>
</tbody>
</table>
Nitrogen and Sulfur air pollutants

<table>
<thead>
<tr>
<th>Selected projects</th>
<th>Report No.</th>
<th>Pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emissions reduction through analysis, modelling and control – ERAMAC</td>
<td>23333</td>
<td>NO$_x$, SO$_2$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VOC, PAH, PCB</td>
</tr>
<tr>
<td>Control of nitrogen oxide emission at the electric arc furnace – CONOX</td>
<td>25078</td>
<td>NO$_x$</td>
</tr>
</tbody>
</table>
## Statistics

<table>
<thead>
<tr>
<th>Period</th>
<th>No. of EAF Projects</th>
<th>Projects</th>
<th>Projects</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1991 - 2016</td>
<td>67</td>
<td>Topic 5</td>
<td>9</td>
<td>13 %</td>
</tr>
<tr>
<td>1991 - 2009</td>
<td></td>
<td>Air pollution</td>
<td>6</td>
<td>9 %</td>
</tr>
<tr>
<td>1991 - 2007</td>
<td></td>
<td>Organic pollution</td>
<td>5</td>
<td>7 %</td>
</tr>
<tr>
<td>2003 - 2009</td>
<td></td>
<td>NO$_x$, SO$_2$</td>
<td>2</td>
<td>3 %</td>
</tr>
</tbody>
</table>
Optimization of environment and related energy utilization in scrap-based steelmaking (Phase I) [16662]

= first study on the formation of PCDD/F and measurements at an EAF

**Literature research:**
PCDD/F formation at municipal waste incineration industry was known. The knowledge was transferred to electric steelmaking. PCDD/Fs are primarily formed at temperatures between 200 °C and 450 °C. Decomposition of PCDD/Fs is obtained by complete combustion in an oxygen rich atmosphere if sufficient time, temperature (> 650 °C) and turbulence are provided. To prevent the de novo synthesis after post-combustion, the off-gas has to be cold down rapidly.

**Measurements:**
The surveys were performed in 1992 and early part of 1993. In the hot gas duct the dioxin concentration varies between 1 and 32 ng I-TEQ/Nm³ with a median of approx. 10 ng I-TEQ/Nm³\textsubscript{flue gas}. In relation to the production this is approximately 12,000 ng I-TEQ/ton\textsubscript{scrap}. There is a good correlation between fly ash and dust concentration and dioxin concentration in the off-gas from the bagfilter.
Optimization of environment and related energy utilization in scrap-based steelmaking (Phase II) [18556]

= first study about PCDD/F control

Three concepts were tested at Det Danske Stålvalseværk A/S:

1. **catalytic destruction** of the dioxin
   → not possible due to the high dust concentration. On the cleangas side the method is possible but economical uninteresting, as the catalysts working temperature must be 350 °C.

2. injection of **pulverised coke** in the flue gas prior to the bag filter
   → absorption very efficient.

3. destruction of dioxin through combustion
   → possible, but higher costs.
Effects of operational factors on the formation of toxic organic micropollutants in EAF steelmaking [21432]

Initial situation in 2001:
Emission limits for some organic pollutants are already applied in some European countries. It is expected that these will become tighter and more uniformly applied across the whole of the EU.

Operational factors that influence the formation of PAHs, PCBs and PCDD/Fs:

- Strong correlation between the concentrations of PCDD/Fs and WHO-12 PCBs, with the I-TEQ of PCDD/Fs being approx. 16.5 times higher than that of WHO-12 PCBs. This suggests that the formation mechanisms of PCBs and PCDD/Fs are linked.
- PCDFs contributed typically 80 to 87% to the overall I-TEQ concentration, especially 2,3,4,7,8-PeCDF with more than 50% at the EAFs from CORUS UK Ltd.
- Scrap quality (concentration of PVC and cutting oils) had a significant influence on PCDD/Fs emission.
- More than 90% of the PCDD/Fs, 60-70% of WHO-12 PCBs and 20-30% of PAHs reported to the dust. So, PCBs and PAHs are generally more volatile than PCDD/Fs.
Effects of operational factors on the formation of toxic organic micropollutants in EAF steelmaking [21432]

Investigation of formation and destruction of VOC in a pre-heating shaft with measurements:
- More than 95 % of the total VOC emission occur within the first 30 minutes of the trial duration (2 h).
- The relative amount of VOC produced is independent of the oil concentration on scrap. So, the carbon content of the oil is pyrolysed to non-volatile elementary carbon remaining on the scrap surface.
- Oxidative destruction of VOC is impossible via oxygen enrichment of the pre-heating gas.

Investigation of reversible adsorption on technical plastics:
- PP powder has better PCDD/F absorption capacity and is cheaper than PP granules (5 mm spheres)
- PP absorbents are not applied, because the absorption rates are only acceptable in narrow temperature range of 90 up to 120 °C. Other adsorbents such as a activated carbon or lignite coke are effective over a wide temperature range.
Emissions reduction through analysis, modelling and control – ERAMAC [23333]

Evaluation of sampling and analytical measuring methods for VOC, PAH and PCB in processes of coke-making, sintering, EAF and coating lines:
- sample gas analysed with thermal desorption, gas chromatography, mass spectrometry (TD-GC-MS)
- possible in off-gases or in ambient air

Measurements in ambient air:
- EAF Sidenor Basauri
- VOC, PAH, PCB, dust, NO\textsubscript{x}, SO\textsubscript{2} measurements for data basis for models
- measurements in stack and approx. 600 m from stack: NO\textsubscript{x} and SO\textsubscript{2} below emission limits

Soft-sensing predictive emissions monitoring system (PEMS):
- VOC, PCB, PAH, NO\textsubscript{x}, SO\textsubscript{2} and dust emissions should be predicted
- sinter plant, coke oven and EAF
- Dynamic soft-sensors were developed for continuous measurements and static models for heat based data.
- CO\textsubscript{2} and O\textsubscript{2} could be predicted; VOC and NO\textsubscript{x} prediction needs more research
Development of catalytic metal filters for simultaneous removal of organic compounds and particulate matter from EAF fumes – CATIA [23737]

Initial situation:
Combustion and rapid cooling of polluted off-gases are expensive and produce greenhouse gases.

Objective:
Development of a FeCrAl filter able to collect dust and destroy PCDD/F, VOC, PCB and PAH at high temperature at a pilot plant at exhaust of the combustion chamber of an EAF

Results:

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Upstream values</th>
<th>Outlet values</th>
<th>Abatement efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust</td>
<td>6,300 to 7,300 mg/Nm³</td>
<td>12 to 69 mg/Nm³</td>
<td>99.3 to 99.8 %</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>37 to 73 ng I-TEQ/Nm³</td>
<td>0.17 to 0.79 ng I-TEQ/Nm³</td>
<td>99 %</td>
</tr>
<tr>
<td>PAH</td>
<td>77 to 333 μg/Nm³</td>
<td>11 to 23 μg/Nm³</td>
<td>70 to 97 %</td>
</tr>
</tbody>
</table>
Development of catalytic metal filters for simultaneous removal of organic compounds and particulate matter from EAF fumes – CATIA [23737]

The eight produced FeCrAl filter cartridges before catalytic activation
Control of nitrogen oxide emission at the electric arc furnace – CONOX [25078]

Initial situation: missing basic data

Objectives:
1. measurements of NOₓ emissions and other off-gas components (CO, CO₂, H₂, O₂) of industrial EAFs at the EAF elbow and in the dedusting system
2. additional investigation of NOₓ formation under well defined atmosphere conditions in laboratory and pilot EAFs
3. modelling of NOₓ emission in the EAF vessel and the post combustion unit of the exhaust gas system by means of thermochemistry of plasma gas species and CFD simulation of post-combustion
Control of nitrogen oxide emission at the electric arc furnace – CONOX [25078]

What do we mean with ‘NO\textsubscript{x}’?
→ Nitrogen Oxides NO\textsubscript{x}: NO, NO\textsubscript{2}, N\textsubscript{2}O

> 90 %

Possible NO\textsubscript{x} formations:

**Thermal NO\textsubscript{x}**
- O + N\textsubscript{2} ⇔ NO + N
- N + O\textsubscript{2} ⇔ NO + O
- N + OH ⇔ NO + H

**Fuel NO\textsubscript{x}**
- 2\left[N\right]_{\text{fuel}} + O\textsubscript{2} → 2NO

**Prompt NO\textsubscript{x}**
- CH + N\textsubscript{2} → HCN + N... → N\textsubscript{2}
Control of nitrogen oxide emission at the electric arc furnace – CONOX [25078]

Sources of NO$_x$ in EAF:
1: Electric arc with plasma temperatures of up to 10,000 K
2: Burners with prompt and thermal NO$_x$ formation at high temperatures, formation of fuel-NO$_x$ from coal
3, 4: Post combustion leading to thermal NO$_x$ formation
Control of nitrogen oxide emission at the electric arc furnace – CONOX [25078]

Measurements at a pilot EAF (RWTH-IOB):

- closed 600 kW pilot arc furnace in AC or DC operating mode
- 150 kg steel and 20 kg slag
- arc length between 70 to 200 mm
Control of nitrogen oxide emission at the electric arc furnace – CONOX [25078]

Results of measurements at pilot EAF (RWTH-IOB):

- High NO\textsubscript{x} concentrations in the off-gas correlate with high O\textsubscript{2} content of the off-gas.
- An increasing CO concentration in the off-gas leads to low NO\textsubscript{x} concentrations.
- Carbon blowing to foam the slag in general has a positive effect on the NO\textsubscript{x} emissions. The amount of carbon blown has no further influence on the NO\textsubscript{x} emissions.
- Slag foaming practice for carbon/tool steel grades leads to significantly higher carbon content and lower NO\textsubscript{x} emissions for these heats.
Control of nitrogen oxide emission at the electric arc furnace – CONOX [25078]

CFD simulation:

- modelling of gas flow and air intake inside the EAF vessel and in the post combustion zone of the primary dedusting system
- gas chemistry, gas flow patterns and NO\textsubscript{x} formation due to the electric arc and in post-combustion zones
- gave new information regarding the position of off-gas measurement probes
Control of nitrogen oxide emission at the electric arc furnace – CONOX [25078]

Results of measurements at industrial EAFs:

- 2 standard EAFs (DEWG, RIVA) and a Consteel process (ORI Martin)
- Same results as at laboratory plant.

Layout of the off-gas analysis system
Control of nitrogen oxide emission at the electric arc furnace – CONOX [25078]

Best practices to reduce the oxygen supply in the EAF:

- Delay of the oxygen injection after arc ignition.
- Use of inert carrier gas for the dust injection into the furnace.
- Keeping the slag door closed if possible to maximise the airtightness of the EAF.
- Variable control of the off-gas volume flow rate to minimise the amount of leak air in the furnace.
Organic pollutants

PCDD/F emissions are very important and so regulated strictly. The limit value is 0.1 ng I-TEQ/Nm³.

VOC emissions are important when scrap preheating is applied. VOCs are usually measured as TOC (total organic carbon). The limit for the average daily emission is 10 mg/Nm³.

PAH emissions target value is 1 ng/Nm³.

PCB is regulated strictly. Regulations, for example the end-of-life electric equipment management, have greatly helped to prevent the introduction of items which contains PCB (for instance small capacitors in several technical devices like washing machines, dryers, cooker hoods, oil burners, fluorescent lamps, etc). However, PCB emissions are less important than the emission of PCDD/F.
Organic pollutants

Basis of the abatement is - of course - the exhausting of all polluted off-gas flows.

Post-combustion with adequate retention time, turbulence and temperature (the three Ts) destroys every organic compound. To prevent the de novo synthesis of PCDD/F, it is essential to have a rapid cooling (quenching) of the fumes as soon as possible after post-combustion to a temperature of below 250 °C.

Post-combustion with additional burners consumes considerable quantities of energy (in the order of 30 kWh/t). Since the hot off-gases need to be quenched to prevent de novo synthesis of PCDD/F, the energy cannot be recovered. The water consumption for quenching can be up to 40 t per hour.

PCDD/F and VOC (PAH and PCB not) can be particle-bound. Typical adsorbents are activated carbon, pulverised activated lignite coke or mixtures of these with lime. Abatement in bag filter.
NO\textsubscript{x} and SO\textsubscript{2} 
→ are not of high relevance in EAF steelmaking and do not need special consideration
Thank you for your attention!

Contact:

RWTH Aachen University
Department for Industrial Furnaces and Heat Engineering
Karima Gandt
Kopernikusstraße 10
52074 Aachen
Germany

gandt@iob.rwth-aachen.de
www.iob.rwth-aachen.de