Towards improvement of heavy metals emission assessment methodology from cement production in EMEP/EEA AEI Guidebook

Belarus contribution to EMEP in-kind for 2011

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Included in presentation:

- Cement production in the AEIGB: tiers, Efs;
- PM and HM emission from cement: WebDab data;
- GB EFs versus derived EFS;
- Proposed algorithms of HM emission calculation (Tier 3);
- Heavy metals flows in cement production;
- Heavy metals in dust from cement production;
- Conclusions.
Cement production is one of the key sources of PM and HM emission

- in EMEP region the share of cement production in total PM make up 12%, up to 48% in certain countries (WebDab);
- cement production provide about 10% of global Hg emission (UNEP, 2008);
- in Belarus cement production responsible for 85% of Hg emissions, 8% of total PM emissions from stationary sources.
Two chapters:

1.A.2.f - Manufacturing industries and construction (combustion)

2.A.1 - Cement production

- 1.A.2.f: Tier 1 – EF only for fuel combustion
- Tier 2 – EF without specification of technology, fuel, raw materials, efficiency of abatement etc.

Cement production in the AEI Guidebook

Table 3-24 Tier 2 emission factors for source category 1.A.2.1, Cement production

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>0.005</td>
<td>g/t</td>
<td>in PM2.5</td>
</tr>
<tr>
<td>CO</td>
<td>0.01</td>
<td>g/t</td>
<td></td>
</tr>
<tr>
<td>SO2</td>
<td>0.005</td>
<td>g/t</td>
<td></td>
</tr>
<tr>
<td>NMVOC</td>
<td>0.002</td>
<td>g/t</td>
<td></td>
</tr>
</tbody>
</table>

Heavy metals

Assumed that HM are from fuel combustion; in what phase?
Comparative values of heavy metals EFs in 1.A.2.f chapter

Hg > Pb ?
Cement production in the AEI Guidebook cont.

2.A.1

- According to the text Tier 1 is applicable only for the processes of raw materials preparation and cement handling.
- TSP, PM10 and PM2.5 is accounted in this chapter only.

Tier 2 emission factors for EECCA only

**Table 3.1 Tier 1 emission factors for source category 2.A.1 Cement production**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Value</th>
<th>Unit</th>
<th>Lower</th>
<th>Upper</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSP</td>
<td>220</td>
<td>g/Mg cement produced</td>
<td>110</td>
<td>440</td>
<td>European Commission (2007)</td>
</tr>
<tr>
<td>PM10</td>
<td>200</td>
<td>g/Mg cement produced</td>
<td>100</td>
<td>400</td>
<td>European Commission (2007)</td>
</tr>
<tr>
<td>PM2.5</td>
<td>110</td>
<td>g/Mg cement produced</td>
<td>55</td>
<td>220</td>
<td>European Commission (2007)</td>
</tr>
</tbody>
</table>

**Table 3.2 Tier 2 emission factors for source category 2.A.1 Cement production, wet process ktha**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Value</th>
<th>Unit</th>
<th>Lower</th>
<th>Upper</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSP</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM10</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM2.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table 3.3 Tier 2 emission factors for source category 2.A.1 Cement production, dry process ktha**

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Value</th>
<th>Unit</th>
<th>Lower</th>
<th>Upper</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSP</td>
<td>2.5</td>
<td>g/Mg cement produced</td>
<td>1.7</td>
<td>3.3</td>
<td>Kukama (2009)</td>
</tr>
<tr>
<td>PM10</td>
<td>0.5</td>
<td>g/Mg cement produced</td>
<td>0.1</td>
<td>1.9</td>
<td>Kukama (2009)</td>
</tr>
<tr>
<td>PM2.5</td>
<td>0.34</td>
<td>g/Mg cement produced</td>
<td>0.06</td>
<td>1.4</td>
<td>Kukama (2009)</td>
</tr>
</tbody>
</table>

HM – in 1.A.2.f
Derived TSP and HM EFs (on the basis of reported emission data - WebDab) vs GB EFs (2006)

Graphs showing EFs for TSP, Pb, Hg, and Zn for various countries (DE, RO, NO, CH, CY, HU, HR, UA, MD, LT, LV, BE) compared to GB EFs (2006).
Derived TSP EFs and PM abatement efficiency (2006)
Large heterogeneity of implied EFs for dust and HM between countries;

Heterogeneous relations between dust and HM Efs;

No indication that Tier 2 EFs from Guidebook are used;

Current methodology is not sufficient for reliable emission inventory of HM emission from cement production;

Sharing of emission from cement between two chapter is not convenient for inventory and review purposes;

Accounting of PM independently from HM is irrational;

For HM emission inventory from cement production heavy metals input flows should be accounted in line with reliable abatement efficiency assessment.
Possible approaches to improvement of heavy metals emission assessment from cement

Tier 2
Based on emission factors of heavy metals for groups of technology/abatement (proposed earlier - not described here)

Tier 3
Based on heavy metal content in dust
Based on material balance (not described here)
A proposal of Tier 3 simple approach on HM emission assessment based on heavy metal content in dust

\[ E_{ij} = \sum (L_i \cdot C_{ij} / (1 - r_i)) \]

where:
E_{ij} – emission of heavy metal i from an installation type j, g
L_j – TSP (dust) emission from installation (source) j, t;
C_{ij} – heavy metal j content in dust from installation j, g/t;
r_i – the share of metal i emitted in gas phase (0.5 – for Hg).
Data sources

Three cement plants in Belarus were investigated;

Data on technologies, types and volumes of raw materials, additives, fuels, sources of emissions, abatement and efficiency, pollutants emissions was analyzed;

Samples of raw materials, raw feed, clinker, cement and dust from ESPs were collected and analysed.
Sources and pathways of heavy metals in cement making process

Raw materials:
- 1.5 to 1.7 tonnes of raw materials per tonne of clinker are used; all natural raw materials (chalk, clay, marl, limestone) contain heavy metals;
- industrial waste (ash, slag, pyrite cinder, dust of metallurgical process etc.) play an important role in cement production;
- industrial waste are used for both processes: clinker roasting and clinker milling.

Fuel:
- approximately 2.9 to 6.7 GJ of energy per tonne clinker are used;
- different fuel are used, including waste;
- the general tendency in the world – increasing of co-incinerating of waste; in Europe their share vary from 2% (Spain) to 72% (the Netherlands).
Input of heavy metals into technological process with raw materials and fuel was assessed.

For Belarus two main types of secondary raw materials were taken into account: pyrite cinder and dust of electrometallurgical steel plant.
It was confirmed that secondary raw materials provide main input of HM into the process; thus, dust from metallurgical plant provide up to 96-98% of Cd, Pb and Zn;

Primary raw materials as well as secondary fuels play also important role in balance of heavy metals;

Regular fuels provide 2-8% of the total input of heavy metals.
Input of raw materials and secondary fuels into heavy metals pathway into cement making process
(main fuel is natural gas)

Secondary raw materials:
Pyrite cinders

- **Hg**
  - 48% from natural raw materials
  - 1% from industrial waste in raw mix
  - 1% from additives to clinker
  - 50% from combustion of tyres

- **Cd**
  - 52% from natural raw materials
  - 26% from industrial waste in raw mix
  - 1% from additives to clinker
  - 21% from combustion of tyres

- **Pb**
  - 84.6% from natural raw materials
  - 8.0% from industrial waste in raw mix
  - 0.5% from additives to clinker
  - 6.9% from combustion of tyres

- **Zn**
  - 73% from natural raw materials
  - 2% from industrial waste in raw mix
  - 8% from additives to clinker
  - 17% from combustion of tyres
Secondary raw materials: Dust of steel plant

- **Hg**
  - 85.5%
  - 14.2%
  - 0.2%
  - 0.1%

- **Cd**
  - 96.6%
  - 3.2%
  - 0.1%
  - 0.1%

- **Pb**
  - 97.8%
  - 0.0%
  - 2.0%
  - 0.2%

- **Zn**
  - 96.1%
  - 2.7%
  - 0.0%
  - 1.2%
Average heavy metals content in dust from cement production

- **As**, **Cd**, **Cr**, **Cu**, **Ni**

- **Pb**, **Zn**

- **Wet process, pyrite cinder**
- **Dry process, dust from steel plant**
<table>
<thead>
<tr>
<th>Raw materials</th>
<th>Index</th>
<th>As (mg/kg)</th>
<th>Cd (mg/kg)</th>
<th>Cr (mg/kg)</th>
<th>Cu (mg/kg)</th>
<th>Hg (mg/kg)</th>
<th>Ni (mg/kg)</th>
<th>Pb (mg/kg)</th>
<th>Zn (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>Maximum</td>
<td>15</td>
<td>2</td>
<td>184</td>
<td>57</td>
<td>0.1</td>
<td>131</td>
<td>151</td>
<td>229</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>3</td>
<td>0.2</td>
<td>14</td>
<td>11</td>
<td>0.04</td>
<td>18</td>
<td>18</td>
<td>30</td>
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<tr>
<td>Marl</td>
<td>Maximum</td>
<td>12</td>
<td>0.5</td>
<td>71</td>
<td>35</td>
<td>0.1</td>
<td>57</td>
<td>57</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>6</td>
<td>0.3</td>
<td>28</td>
<td>12</td>
<td>0.03</td>
<td>16</td>
<td>12</td>
<td>48</td>
</tr>
<tr>
<td>Clay</td>
<td>Maximum</td>
<td>100</td>
<td>1</td>
<td>260</td>
<td>285</td>
<td>0.5</td>
<td>236</td>
<td>219</td>
<td>304</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>14</td>
<td>0.2</td>
<td>85</td>
<td>43</td>
<td>0.2</td>
<td>63</td>
<td>25</td>
<td>78</td>
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<tr>
<td>Metallurgical waste</td>
<td>Maximum</td>
<td>1200</td>
<td>17900</td>
<td>200000</td>
<td>12600</td>
<td>10</td>
<td>80000</td>
<td>570000</td>
<td>350000</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>151</td>
<td>109</td>
<td>3284</td>
<td>1872</td>
<td>2</td>
<td>830</td>
<td>4698</td>
<td>21641</td>
</tr>
<tr>
<td>Iron ore</td>
<td>Maximum</td>
<td>1200</td>
<td>15</td>
<td>1400</td>
<td>-</td>
<td>1</td>
<td>815</td>
<td>8700</td>
<td>9400</td>
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<tr>
<td></td>
<td>Average</td>
<td>37</td>
<td>6</td>
<td>495</td>
<td>1520</td>
<td>0.5</td>
<td>331</td>
<td>350</td>
<td>3288</td>
</tr>
<tr>
<td>Fuel ash</td>
<td>Maximum</td>
<td>42</td>
<td>2.3</td>
<td>450</td>
<td>110</td>
<td>1.4</td>
<td>240</td>
<td>200</td>
<td>470</td>
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<tr>
<td></td>
<td>Average</td>
<td>6.6</td>
<td>0.6</td>
<td>190</td>
<td>32</td>
<td>0.3</td>
<td>23</td>
<td>25</td>
<td>94</td>
</tr>
<tr>
<td>Gypsum/ anhydrite</td>
<td>Maximum</td>
<td>3.5</td>
<td>2.3</td>
<td>27.3</td>
<td>12.8</td>
<td>1.3</td>
<td>14.5</td>
<td>20.5</td>
<td>59</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>1.5</td>
<td>0.15</td>
<td>8.8</td>
<td>7</td>
<td>0.1</td>
<td>5.5</td>
<td>7</td>
<td>18</td>
</tr>
<tr>
<td>Blast-furnace slag</td>
<td>Maximum</td>
<td>1</td>
<td>1</td>
<td>75</td>
<td>10</td>
<td>1</td>
<td>10</td>
<td>21</td>
<td>280</td>
</tr>
<tr>
<td></td>
<td>Average</td>
<td>0.8</td>
<td>0.7</td>
<td>25</td>
<td>5.2</td>
<td>0.6</td>
<td>5</td>
<td>6</td>
<td>38</td>
</tr>
</tbody>
</table>
Contribution of raw materials and secondary fuels into heavy metals input into cement (main fuel is coal and secondary wastes, incl. tyres) – UBA (2003)

- **Cd**
  - Primary raw materials: 48%
  - Secondary fuels: 29%
  - Interground additives: 8%
  - Regular fuels: 3%

- **Cu**
  - Primary raw materials: 52%
  - Secondary fuels: 6%
  - Interground additives: 2%
  - Regular fuels: 3%

- **Pb**
  - Primary raw materials: 70%
  - Secondary fuels: 16%
  - Interground additives: 3%
  - Regular fuels: 8%

- **Zn**
  - Primary raw materials: 38%
  - Secondary fuels: 37%
  - Interground additives: 3%
  - Regular fuels: 2%
Comparative content of heavy metals in clinker
# As a proposal for GB: HM content in dust from cement production (by stages)

<table>
<thead>
<tr>
<th>Process</th>
<th>Secondary raw materials (main)</th>
<th>As</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Hg</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roasting</td>
<td>Pyrite cinder</td>
<td>35</td>
<td>15</td>
<td>15</td>
<td>65</td>
<td>0.02</td>
<td>15</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>Roasting</td>
<td>Dust of electrometallurgical plant</td>
<td>3</td>
<td>15</td>
<td>10</td>
<td>40</td>
<td>0.2</td>
<td>17</td>
<td>250</td>
<td>3500</td>
</tr>
<tr>
<td>Clinker milling</td>
<td>Pyrite cinder</td>
<td>20</td>
<td>1.5</td>
<td>5</td>
<td>95</td>
<td>0.01</td>
<td>15</td>
<td>25</td>
<td>250</td>
</tr>
<tr>
<td>Clinker milling</td>
<td>Dust of electrometallurgical plant</td>
<td>3</td>
<td>2.5</td>
<td>6.5</td>
<td>18</td>
<td>0.01</td>
<td>15</td>
<td>40</td>
<td>1500</td>
</tr>
</tbody>
</table>
Share of different shops in TSP emissions from cement production

Wet process
- Storage of raw material: 1%
- Cement storage and package: 4%
- Grinding: 8%
- Roasting: 87%

Dry process
- Storage of raw material: 2%
- Grining: 7%
- Roasting: 91%
Conclusions

- A great deal need to be improved in cement chapter(s) to make them effective and user friendly;
- A simple algorithm is proposed for HM emission inventory as a Tier 3, accompanied by a table of HM content in cement dust;
- Advantages of this algorithm:
  - cost-effective method for emission assessment on facility and sector level;
  - heavy metals content values in dust from different data sources may be used;
  - harmonization of PM and HM emission is provided.
Thank you for your attention!