Heavy Metal Separation from Flue Gas Scrub Water with TMT15®

McIlvaine Company Hot Topic Hour on FGD Wastewater Treatment

Rüdiger Peldszus
June 16, 2011
An attractive company

- One of the global leaders in its core specialty chemicals business
- Investments in the energy and real estate sectors

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sales 2010</td>
<td>€13.3  billion</td>
</tr>
<tr>
<td>Chemicals</td>
<td>€12.9  billion</td>
</tr>
<tr>
<td>Real Estate</td>
<td>€0.4   billion</td>
</tr>
<tr>
<td>EBITDA</td>
<td>€2.365 billion</td>
</tr>
<tr>
<td>Profitability (EBITDA margin)</td>
<td>17.8%</td>
</tr>
<tr>
<td>Return on capital employed (ROCE)</td>
<td>15.0%</td>
</tr>
<tr>
<td>Employees 2010</td>
<td>34,407</td>
</tr>
</tbody>
</table>
Trimercapto-s-triazine

**Representative Product:**

TMT 15®, Evonik Industries AG

**Application:**

Heavy metal precipitation agent

**Industries:**

- Combustion/Incineration Plants
- Metalworking/Chemical Industry
- Mining

**Structure:**

![Chemical Structure](image)

**Product Data:**

- **CAS-No.:** 17766-26-6
- **Commodity:** aqueous solution
- **Appearance:** light yellow liquid
- **Odor:** almost odorless

(MSDS Evonik Degussa GmbH)
Reaction of TMT 15® with Heavy Metals (e. g. Mercury)

$$3 \text{Hg}^{2+} + 2 \text{TMT}^{3-} = \text{Hg}_3\text{TMT}_2$$

- **C** = TMT 15® (C$_3$S$_3$N$_3$ Na$_3$)
- **M** = Heavy Metal e. g. Hg$^{2+}$
Waste Water Treatment

Neutralization
fails in the presence of Complexes

Alternative Process:
Precipitation with TMT 15®
Coal/garbage contains heavy metals which are set free during combustion

→ Main problem:
  Toxic Mercury and Cadmium

• Elimination of toxic heavy metal out of flue gas scrub water by precipitation

• Evonik’s proven application in several hundred combustion plants worldwide

• Minimization of mercury emission in flue gas
**TMT 15® at Coal Fired Power Stations**
- Flue gas wash water treatment

**Typical treatment:**
- Neutralisation to pH 9 → Hydroxide precipitation
- Addition of TMT 15® → Mercury precipitation
- Flocculation with Polyelectrolyte
  (sometimes additional ferric dosage to optimize the flocculation)
- Particle removal by circular or lamellar clarifier
- Fine particle removal e.g. by sand filter
- Additional treatment like biological processes possible

* FGWW = Flue Gas Wash Water
## Flue Gas Scrub Water treatment - Coal fired power station

<table>
<thead>
<tr>
<th>TMT 15 Dosage</th>
<th>Pb</th>
<th>Cd</th>
<th>Cu</th>
<th>Ni</th>
<th>Hg</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>ml/m³</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
<td>mg/l</td>
</tr>
<tr>
<td>Untreated Sample</td>
<td>-</td>
<td>1.4</td>
<td>0.02</td>
<td>0.29</td>
<td>0.44</td>
<td>2.2</td>
</tr>
<tr>
<td>Sample 1</td>
<td>0</td>
<td>0.44</td>
<td>0.018</td>
<td>0.03</td>
<td>0.4</td>
<td>1.22</td>
</tr>
<tr>
<td>Sample 2</td>
<td>30</td>
<td>0.02</td>
<td>&lt; 0.0006</td>
<td>0.02</td>
<td>0.4</td>
<td>&lt; 0.0002</td>
</tr>
<tr>
<td>Sample 3</td>
<td>50</td>
<td>&lt; 0.02</td>
<td>&lt; 0.0006</td>
<td>0.035</td>
<td>0.38</td>
<td>&lt; 0.0002</td>
</tr>
<tr>
<td>Sample 4</td>
<td>70</td>
<td>&lt; 0.02</td>
<td>&lt; 0.0006</td>
<td>&lt; 0.02</td>
<td>0.38</td>
<td>&lt; 0.0002</td>
</tr>
<tr>
<td>Sample 5</td>
<td>100</td>
<td>&lt; 0.02</td>
<td>&lt; 0.0006</td>
<td>0.03</td>
<td>0.35</td>
<td>&lt; 0.0002</td>
</tr>
<tr>
<td>47 VwV*</td>
<td>0.2</td>
<td>0.05</td>
<td>0.5</td>
<td>0.5</td>
<td>0.03</td>
<td>1.5</td>
</tr>
</tbody>
</table>

### Treatment Conditions:
Several 0.25 l samples of neutral flue gas scrub water (pH = 5.6) set to pH 9 with NaOH, different quantities of TMT15® added (30 minutes reaction time), flocculated (Polyelectrolyte, approx. 3 ml 0.1% sol./l), after 1.5 h sedimentation time filtered by a 0.2 membrane filter and the residual concentration of heavy metals analyzed by ICP.

* 47. German administrative fiat
TMT 15® at Coal Fired Power Stations
- Hard Facts / Instance plant I

- CFP Station, Germany
- Total 580 MW (2 blocks)
- German + Import Hard Coal
  (Summer ~125 t/h : Winter ~190 t/h)
- Wet FGD system with wash water treatment
- Blowdown: 15-20 m³/h flue gas scrub water
- TMT 15® Addition: 20 ml TMT 15®/m³ blowdown
  = 2.5 ml TMT 15®/t coal
- Residual mercury content: < 0.2 µg Hg/l
- Residual cadmium content: < 0.2 µg Cd/l
- TMT 15® application since FGD start up in 1988

CFP = Coal fired power station
TMT 15® at Coal Fired Power Stations - Hard Facts / Instance plant II

- CFP Station, Germany, 356 MW
- Import Hard Coal, 120 t/h
- SCR + wet limestone FGD system with wash water treatment
- Blowdown: 20 m³/h flue gas scrub water
- TMT 15® Addition: 50 ml TMT 15®/m³ blowdown = 8 ml TMT 15®/t coal
- Residual mercury content: < 1 µg Hg/l
- TMT 15® application since FGD start up in 1989

CFP = Coal fired power station
Heavy Metal Separation with TMT 15\textsuperscript{®}

Classification
Toxicity
Handling Safety
Benefits
## TMT 15®
### Classification / Toxicity

### Classification

<table>
<thead>
<tr>
<th>CAS-RN</th>
<th>17766-26-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commodity</td>
<td>15% solution</td>
</tr>
<tr>
<td>GHS-Labelling</td>
<td>Warning</td>
</tr>
<tr>
<td>Transport-regulations</td>
<td>No dangerous good</td>
</tr>
</tbody>
</table>

### Toxicity

<table>
<thead>
<tr>
<th>Acute tox.</th>
<th>7 878</th>
</tr>
</thead>
<tbody>
<tr>
<td>LD$_{50}$ * (rat, mg/kg)</td>
<td></td>
</tr>
<tr>
<td>Lethal conc.</td>
<td>12 000</td>
</tr>
<tr>
<td>LC$_{0}$ ** (fish, mg/l)</td>
<td></td>
</tr>
<tr>
<td>Mutagenity</td>
<td>no</td>
</tr>
<tr>
<td>Products of decomposition</td>
<td>none</td>
</tr>
</tbody>
</table>

* LD$_{50}$ = Concentration where 50% of the rats die
** LC$_{0}$ = Concentration where no fish dies
Best Available Techniques (BAT) for Waste incineration

Abstract of: WI_BREF_FINAL / Chapter 5.1 „Generic BAT for all waste incineration“

Therefore, in combination with the additional waste stream specific BAT listed in later sections of this chapter, in order to provide for levels of performance that are generally compatible with BAT, in general BAT for waste incineration is considered to be:

48. where wet flue-gas treatment is used:

   e. the use of sulphides (e.g. M-trimercaptotriazine) or other Hg binders to reduce Hg (and other heavy metals) in the final effluent, as described in 4.5.11
Abstract of: WI_BREF_FINAL

Chapter 3.3.5 Hazardous waste incineration plants – European survey data
- Mercury

Mercury in the effluent originates, of course, from mercury contained in the waste. It is common practice that incinerators apply an input limit for mercury over a time period.

For one installation equipped with wet gas scrubbing, it is calculated that the total mercury input via the waste, amounts to 2000 kg/yr for an installation with an incineration capacity of 100000 t/yr. Taking into account a maximum yearly emitted Hg flow via the waste water of less than 4 kg/yr, a removal efficiency higher than 99.8 % can be reached based on M-trimercaptotriazine precipitation and subsequent efficient removal of the precipitate.
• TMT 15®:
  Proven application in several hundred combustion plants worldwide thereof 135 coal fired power stations

• Residual mercury concentration in treated flue gas wash water in the range of a few µg Hg/l or less can be reached based on precipitation with TMT 15® and a subsequent efficient removal of the precipitate

• Trimercaptotriazine (TMT) is announced from the European Commission as Best Available Techniques (BAT) for waste incineration where wet flue-gas treatment is used too
Heavy metal precipitation
Benefits of TMT 15®

- highly effective in various applications
- proven application and state-of-the-art in combustion plants
- stable heavy metal compounds
- non-toxic and non-hazardous
- safe handling and no unpleasant odor
- good ecological properties
- qualified and “up to date” support
- experienced application and technical competence
Information / Contact

• **TMT 15 Homepage**  www.evonic.com/tmt15

• **Application and Technology**

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