Mercury and Mercury Oxidation

Rich Marsan
April 16, 2013 – WPCA WWT Conference
The Path of Mercury

This diagram shows that the ways to influence the mercury concentration are limited.

Power Plant Process

- Ash
- Byproducts
- Waste Water
- Flue Gas

Mercury can either be prevented from entering the process or has to be removed from the process via ash, waste water, flue gas or byproducts (e.g. gypsum). If byproducts are sold the amount of mercury in them is limited. Regulation limits the amount of mercury discharged via flue gas and waste water.
What is the fate of the Mercury?

Into the Bottom Ash

Out with Flyash

Into the Gypsum Product
“Typical” Mass Balance for Mercury

Clean gas: %
0.2 % HM 1
2 % HM 2
10 % HM 3

Ash:
97 % HM 1
68 % HM 2
5 % HM 3

Gypsum slurry:
2.7 % HM 1
30 % HM 2
85 % HM 3

HM 1 = As, Ag, Ba, Be, B, Cd, etc.
HM 2 = Se
HM 3 = Hg

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Mercury and Air Toxics Standards (MATS)

- EPA finalized the Mercury and Air Toxics Standards (MATS) rule in December 2011, covering mercury and hazardous air pollutants (HAPs) like selenium, arsenic and others
- Existing coal- and natural gas-fired plants face a compliance date of April 2015, with a 'broadly available' one-year extension
- First time mercury has been regulated at a national level for power plants, although ~16 states were already phasing in limits roughly similar to MATS

<table>
<thead>
<tr>
<th></th>
<th>Filterable PM&lt;sup&gt;a&lt;/sup&gt;</th>
<th>HCl&lt;sup&gt;b&lt;/sup&gt;</th>
<th>SO&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing units (higher grade coals)</td>
<td>3*10^-2 lb/MMBtu (~45 mg/Nm³)</td>
<td>2*10^-3 lb/MMBtu (~3 mg/Nm³)</td>
<td>0.20 lb/MMBtu (~300 mg/Nm³)</td>
<td>1.2 lb/TBtu (~1.8 ug/Nm³)</td>
</tr>
<tr>
<td>Existing units (lignite)</td>
<td>3*10^-2 lb/MMBtu (~45 mg/Nm³)</td>
<td>2*10^-3 lb/MMBtu (~3 mg/Nm³)</td>
<td>0.20 lb/MMBtu (~300 mg/Nm³)</td>
<td>4.0 lb/TBtu (6 mg/Nm³)</td>
</tr>
</tbody>
</table>

<sup>a</sup> Surrogate for non-mercury HAP metals
<sup>b</sup> Surrogate for acid gas HAP
<sup>c</sup> Surrogate for acid gas HAP for plants operating FGDs
What is the Utility drivers?

What is Driving the New Technology’s?

- **Effluent Discharge Limits of:**
  - Hg: 12 ppt
  - Se: 6 ppb

- **Mercury cannot be removed with typical precipitation**

- **Selenium is extremely water soluble**

- **\( \text{Se}_{\text{IN}} = \text{Se}_{\text{OUT}} \) for Typical Waste Water**
Combustion Process Relevant Reactions

**Formation of Mercury Oxide in the Furnace**

\[2 \text{Hg} + \text{O}_2 \leftrightarrow 2 \text{HgO}\]

**Formation of Elemental Chlorine in the Furnace**

\[4 \text{HCl} + \text{O}_2 \leftrightarrow 2 \text{H}_2\text{O} + 2 \text{Cl}_2\]

**Oxidation of Mercury**

\[\text{Hg} + \text{Cl}_2 \leftrightarrow \text{HgCl}_2\]

These reactions are important for the oxidation of elemental mercury in the furnace and boiler, the generation of Cl\(_2\) and subsequent formation of ionic mercury.
The SCR Oxidation Reaction

- The Vanadium Pentoxide ($V_2O_5$) releases oxygen ($O_2$)
- The flue gas stream contains the following constituents; Nitrous Oxide (NO or NO$_2$), Sulfur Dioxide (SO$_2$) and Mercury (Hg) which compete for the oxygen.
- The preference for the oxygen is:
  - 1$^{st}$ - Nitrogen
  - 2$^{nd}$ - Sulfur Dioxide
  - 3$^{rd}$ - Mercury
- The presence of Ammonia (for the NOx reaction) inhibits the Mercury reaction.

$$NO_x + O_2 + NH_4 \Rightarrow N_2 + H_2O$$
$$Hg^0 + O_2 \Rightarrow Hg^{2+}$$
$$SO_2 + O_2 \Rightarrow SO_3$$
SCR Catalyst Arrangement
New Layer of catalyst on Top Layer

- Results:
  - Ammonia is consumed in the top layer.
  - Lower 2 elevations will produce the oxygen for Mercury Oxidations (also SO$_2$ to SO$_3$ conversion rate)

High levels of oxidation should occur with the Mercury!
SCR Catalyst Arrangement
Depleted Catalyst Reactor

Results:
- Ammonia consumption for NOx removal takes most of the catalyst surface.
- Lower level is the only effective surface for Mercury (also SO2 to SO3 conversion rate).

Low levels of oxidation should occur with this arrangement!
The STEAG Mercury Approach

• This is a 2 Phase Approach
  – Phase 1 - Oxidized Mercury captured in a wet FGD system
  – Phase 2 – Disposition of the Mercury. There are several options.

• STEAG Approach Requirements
  – The Mercury must be in the oxidized state (Hg2+)
  – Wet FGD System
  – Power Activated Carbon (PAC) is added to Wet FGD System
  – Mercury can be removed from the process by:
    • Mercury in the gypsum/dewatered solids
    • Mercury into the waste water filter press
    • Mercury / metals reduced and then removed from system
How is the Mercury Sequestered?

- The FGD liquid does the mercury capture process. Oxidized Mercury is very soluble and
- STEAG adds carbon to the liquid phase of the droplet.
- The mercury the moves into the solid part of the particle remains captured.
- The mercury / carbon in the liquid phase is the important mercury capture.
- Once the mercury bonds to the carbon it cannot convert back to elemental state.
Dosing Skid for PAC:

- Gravity influenced and reliable dosing of PAC from Super Sacks
- Injection of PAC upstream of FGD recycle pump
- PAC consumption depends on FGD blow
down, approx. < 50 kg (100 lbs) per day

Alternative option:
- Manual interval dosing of PAC from bags

Different Injection Points
Simplified wFGD Process without Hydroclones

- **raw gas inlet**
- **pH 5.2 - 5.8**
- **oxideation air**
- **limestone slurry**
- **PAC Injection**
- **mercury**
- **oxidation air**
- **wastewater hydrocyclone**
- **gypsum hydrocyclone**
- **mercury**
- **gypsum < 10% moisture CaSO₄ · 2H₂O**
- **gypsum dewatering**
- **filtrate**

- **clean gas outlet**
- **absorber**
- **mist eliminator**
- **process water**

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Testing Results

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Plant A</th>
<th>Plant B</th>
<th>Plant C</th>
<th>Plant D</th>
<th>Plant E</th>
<th>Plant F</th>
<th>Plant G</th>
<th>Plant H</th>
<th>Plant I</th>
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<tbody>
<tr>
<td>SCR / SNCR</td>
<td>Western Bit.</td>
<td>PRB</td>
<td>PRB</td>
<td>Western Bit.</td>
<td>SNCR</td>
<td>Western Bit.</td>
<td>SNCR</td>
<td>Eastern Bit.</td>
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<tr>
<td></td>
<td>No</td>
<td>SCR</td>
<td>SCR</td>
<td>SNCR</td>
<td>SCR</td>
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<td>Halogen Addition</td>
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<td>CaBr2 Addition (OD)</td>
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<tr>
<td>FGD</td>
<td>W-Sodium</td>
<td>LSFO</td>
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Need for Immediate Compliance

- Accepted by State compliance.
  - By State requirements - Injection at 850 #/hr (5 #/ million acfm)
- Unit sizes 365 MW / 590 MW.
- Temporary PAC Injection System.
- Inject Rate is 6 # / Hr – both units.
- 30 min. per week feed once a week.
- Operational since September 2012.

Savings to this utility for this station is $ 6.6 million per year. System payback is in less than 2 months!
First US Commercial System

- Mid-Western Utility
- 2 units dosed w/1 PAC addition system
- Feed to each unit less than 30 min. per day
- About 300 ft of piping
- PLC control system.
- Injection direct into units
- Back-flush system
Equipment Selection

- Option Chosen: Conti TDS Skid for high throughput dosing
- Super-sack based System – 900#
- Change bag once per week
- Both units dosed in about ½ hr.
- Silo based system available for higher PAC volume users
## Typical Schedule

<table>
<thead>
<tr>
<th>Task Name</th>
<th>Duration</th>
<th>Start</th>
<th>Finish</th>
<th>Predecessors</th>
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<tbody>
<tr>
<td>1 Skid Fabrication</td>
<td>22 wks</td>
<td>11/1/2012</td>
<td>4/3/2013</td>
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<tr>
<td>2 Controls Engineering</td>
<td>3 wks</td>
<td>1/7/2013</td>
<td>1/25/2013</td>
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<td>3 Piping Engineering</td>
<td>5 wks</td>
<td>1/7/2013</td>
<td>2/8/2013</td>
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<tr>
<td>4 Controls Installation</td>
<td>2 wks</td>
<td>4/4/2013</td>
<td>4/17/2013</td>
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<tr>
<td>5 Piping Installation</td>
<td>3 days</td>
<td>2/11/2013</td>
<td>2/22/2013</td>
<td>3</td>
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<tr>
<td>6 Skid Installation</td>
<td>1 wk</td>
<td>4/18/2013</td>
<td>4/22/2013</td>
<td>4</td>
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<tr>
<td>7 Commissioning and Startup</td>
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<td>4/23/2013</td>
<td>4/29/2013</td>
<td>6</td>
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</tbody>
</table>
Removal of the Mercury

• **Decision Cycle**
  - Is the Gypsum being sold?
  - Does Mercury need to be removed?
  - Landfill / Product Liability?

• **Hydro-cyclones is the Mercury Separation System**
  - Mercury to the Waste Water Treatment
  - Hydro-cyclone separation equipment may need 2 stage separation system
  - Adjustments in the separation equipment may be needed

From Absorber

1st Stage

2nd Stage

To Waste Water Treatment

To Gypsum Drying
FGD Waste Water Treatment Details

**Step 1**
- **Oxidation**
  - pH = 6.5
  - NaOCl / ClO₂
- **Flocculation**
  - pH = 6.5
  - Ca(OH)₂, PE
- **Sedimentation**
  - Thickener
- **Filter Press**
  - Slurry Dewatering (incl. PAC)
  - Waste Water Hg < 30 ppb
  - Hg ~ 10 ppm
  - Recycling to Coal > 95 %

**Step 2**
- **Flocculation**
  - pH = 8.5
- **Sedimentation**
  - Organo sulfide (TMT15)
  - FeCl₃, PE
- **Membrane Filter Press**
- **Landfill**
  - Hg: up to 2000 ppm
  - < 5 %
Waste Characterization

Waste minimization

Hg-free sludge to combustion >95%

Hg-containing sludge to landfill <5%

CaSO₄ 18%
CaCO₃ 11%
MnO 4%
Hg 2000 ppm
CaF₂ 13%
AL₂O₃ 7%
Fe₂O₃ 3%
MG(OH)₂ 26%
SiO₂ 16%

CaSO₄ 28%
CaCO₃ 2%
MnO 1%
Hg 3 ppm
CaF₂ 31%
AL₂O₃ 13%
Fe₂O₃ 3%
MG(OH)₂ 2%
SiO₂ 20%
Why STEAG’s mercury technology?

- **Mercury Must be Oxidized for Effective Capture:**
  - No SCR: Calcium Bromide Addition (e.g. Alstom KNX)
  - SCR: Catalyst will do the oxidation
- **The PAC/gypsum mixture can be separated completely using hydrocyclones (gypsum whiteness unaffected).**
- **Ammonia Oxidation and Mercury Oxidation are Competing Reactions**
- **Mercury Oxidation decreases over Time**
- **Costs:**
  - Investment cost of PAC dosing station: TBD/site specific
  - Operating costs: based on blow down rate and cost of PAC