Power Plant Pollution Controls

Green Chemistry Fall 2007

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Power Plant Pollution Controls

1. Power plants and fuels
2. Emission control technologies
3. Are pollution controls green?
Fuels

- Coal is by far the most likely to produce pollution.
- Cleanest to least clean coal types:
  - Anthracite
  - Bituminous
  - Sub-bituminous
  - Lignite
- Natural gas can contain some sulfur, but otherwise is very clean. Only NO$_x$ controls must be used.
US Electricity Energy Flow

All numbers are in quadrillion ($10^{15}$) BTU (1 BTU ≈ 1.05 kJ)

Figure from EIA Annual Energy Review 2006
http://www.eia.doc.gov/emeu/aer/diagram5.html
Coal power plant designs

- Pulverized coal steam boiler
  - High-quality coal is crushed, then burned.
  - Traditional design
- Fluidized-bed
  - Burns at lower temps with limestone directly.
  - Minimizes SO\textsubscript{2} and NO\textsubscript{x} emissions
- Coal gasification
  - Coal is exposed to hot steam and low O\textsubscript{2} conditions.
  - Organic molecules decompose to form syngas.
  - Using gas turbines allows better efficiency.
- All data here is for electricity-generating power plants.
Figure 7-1  Schematic diagram of a typical pulverized coal steam boiler for the generation of electrical power. (Babcock and Wilcox, 1978)

http://www.tva.gov/power/coalart.htm

Heinsohn, R. J.  *Sources and Control of Air Pollution.*
Major Pollutants

- **Nitrogen oxides (NO$_x$)** – from high heat oxidation of atmospheric nitrogen in combustor
- **Sulfur dioxide** – formed from oxidation of sulfur compounds in coal (pyrite and organic)
- **Mercury** – amount depends on the type of coal used
- **Particulates** – includes ash, carbon, and sulfur-containing aerosols
- **Carbon dioxide**
Pollution effects

- Acid rain
- Photochemical smog
- Respiratory disease
- Mercury poisoning
- US Clean Air Act passed 1963
NO$_x$ and Government Regulation

- Government regulations were the driving force behind development of NO$_x$ controls.
- Cost reductions are proportional to technology adoption.

Yeh, Rubin, Taylor, and Hounshell J. Air & Waste Manage. Assoc. 55:1827–1838
Ways to control pollution

- Fuel type and pretreatment
- Combustor alterations
  - Optimization of conditions and inputs in steady state
  - Re-feed inert flue gases into system to dilute oxygen
- Flue gas controls
- Effective measurement of pollution emission
Considerations when adopting control technologies

- Cost to build and maintain
- Energy usage
- Reagents needed to operate
- Byproducts - usable or dumped?
- Effectiveness
- Effect on multiple pollutants – some control technologies can control more than one pollutant.
Coal pretreatment

- Coal washing – grind coal into small pieces and use density to separate it from other minerals.

Combustor Alterations

- Optimization of conditions and inputs in steady state
- Re-feed inert flue gases into system to dilute oxygen
Flue Gas Control Technologies

- Catalytic reduction
- Scrubbers
- Particulate Controls
  - Fabric bag filters
  - Vortex and drop tray
  - Electrostatic precipitators
- Oxidizing/reducing agents
- Adsorbents
- Carbon sequestration
Acronyms

- FGD – flue gas desulfurization
- PCD – particulate control devices
- SCR – selective catalytic reduction
- ESP – electrostatic precipitators
- LNB – low NO\(_x\) burner
- CT – control technology
- CFB – circulating fluidized bed
$\text{NO}_x$
Sources of NO$_x$

- Thermal NO$_x$
  - Formed by high temperature oxidation of atmospheric nitrogen
  - Very sensitive to peak temperature (reciprocating engines)
  - 85% of total NO$_x$

- Prompt NO$_x$
  - Made in reactions of N$_2$ and flame-produced hydrocarbon radicals
  - Occurs in fuel-rich areas of combustor

- Fuel NO$_x$ – formed from nitrogen in the fuel
Combustor Modifications

1. Combustor geometry optimization

2. Flue gas recirculation
   - Dilutes fuel/air mix with flue gas ($O_2$ conc 3.3% is standard)

3. Low $NO_x$ burners (LNB)
   - A type of staged combustion, using fuel-rich and fuel-lean zones to reduce peak temp.
   - These are the least expensive options
   - All work by reducing fuel burning temperature
Figure E7-5  Equilibrium concentrations (ppm) of NO₂ and NO versus temperature (K). Initial conditions % by volume:
SCR – Selective Catalytic Reduction

- The reaction of NO$_x$ and NH$_3$ (or urea) with a catalyst bed at high temperature.
  \[ \text{NO}_x + \text{NH}_3 + \text{O}_2 \rightarrow \text{N}_2 + \text{H}_2\text{O} \]

- Pros & Cons:
  - Eliminates 70-90% of NO$_x$
  - Expensive catalyst with high replacement cost
  - Stoichiometric ammonia or urea is required
  - High sulfur content in flue gases can poison catalyst
  - Can be done non-catalytically (SNCR)
Figure 10-27 Schematic diagram of staged thermal reduction of NO\textsubscript{x} for an electric utility boiler showing nonselective catalytic ammonia injection (NSCR) and in-duct and air-heater applications of selective catalytic reduction (SCR) (with the permission of Wahlco).

SCR Catalysts

- Noble metal catalysts (Pt/Al₂O₃) at low temp
  - Easily poisoned and corroded by sulfur compounds (used in natural gas plants only)
  - Lower Temp
- Base metal catalysts (V₂O₅/TiO₂/other metals)
  - Poisoned by particulates, acids, some metal oxides
  - Toxic: special disposal required
- Zeolites (zeolite/Cu/Fe)
  - High Temp, more NH₃ required
SCR capacity

![Graph showing cumulative GWe from 1980 to 2002 for different regions: World, US, Japan, Germany, and Others. The graph indicates an increase in SCR capacity over time, with a significant rise in the late 1990s.]
## Reduction of NO$_x$

<table>
<thead>
<tr>
<th>Technology</th>
<th>Yeh, Rubin, Taylor, and Hounshell</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustor alterations</td>
<td>30-60%</td>
</tr>
<tr>
<td>SNCR</td>
<td>30-50%</td>
</tr>
<tr>
<td>SCR</td>
<td>70-90%</td>
</tr>
</tbody>
</table>
$\text{SO}_2$
SO$_2$ Flue Gas Scrubbing

- **Dry scrubbing**
  - Ca(OH)$_2$ slurry droplets or solid NaCO$_3$ particles are injected in flue gas stream
  - CaSO$_4$ or Na$_2$SO$_4$ particles are captured by fabric filters with fly ash

- **Wet scrubbing**
  - Limestone slurry reacts to form CaSO$_3$, then CaSO$_4$
  - Corrosive low pH and scaling are produced
  - Large amounts of waste sludge are produced.
Figure 10-29 Schematic diagram of the GE Dry Flue Gas Desulfurization System using lime to remove SO$_2$. The lime reagent enters the system as a slurry. Hot flue gas evaporates water from the slurry and SO$_2$ is adsorbed on the remaining particles of dry reagent. Flyash and the dry reagent are collected by a fabric filter. Additional SO$_2$ is adsorbed as the flue gas passes through the dust cake containing the dry reagent particles. (Figure used by permission of General Electric Environmental Services, Inc.)
Limestone Slurry Forming

- Limestone (CaCO\(_3\)) is converted to form more reactive and soluble calcium hydroxide.
  \[ \text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2 \]
  \[ \text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 \]

- Calcium hydroxide or limestone reacts with sulfur dioxide.
  \[ \text{CaCO}_3 + \text{SO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot 2\text{H}_2\text{O} + \text{CO}_2 \] or
  \[ \text{CaO} + \text{SO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CaSO}_3 \cdot 2\text{H}_2\text{O} \]

- CaSO\(_3\) converts to sulfate in acidic environments with oxygen.
Fluidized Bed Combustors

- Solid coal pieces are uplifted by gas coming from the bottom and burned in.
- Limestone (CaCO$_3$) or dolomite (MgCO$_3$) is added to the dry fuel, which captures sulfur before it leaves the combustor (up to 90%). Na, K, CaCl$_2$ added to increase adsorption.
Heinsohn, R. J.  *Sources and Control of Air Pollution.*
Advantages of FBT

- Uniform, lower temperature throughout the bed
- Complete mixing of fuel and limestone provides good SO$_2$ reduction
- Large interface between gas and solid
- Lower temperatures means much less NO$_x$
- Lower-quality coal and other fuels can be burned.
Catalytic Oxidation of SO$_2$ on Zeolites

- SO$_2$ weakly adsorbs to powdered zeolite in the presence of water vapor. Will release upon heating.

- The SO$_2$ can be oxidized to sulfate by H$_2$O$_2$, making H$_2$SO$_4$.

- Disadvantage: adsorbed CO$_2$ must be washed off with HCl, then D.I. water.

- Adsorption range: 35-72 mg SO$_2$/g zeolite from 290 to 350 K
Experimental Setup
**SO₂ Removal**

- 90% to 98% using wet scrubbers
- Up to 80% using dry scrubbers
- Limited to SO₂ at 2000 ppm

<table>
<thead>
<tr>
<th>Scrubber Type</th>
<th>Unit Size (MW)</th>
<th>Capital Cost ($/kW)</th>
<th>O&amp;M Cost ($/kW)</th>
<th>Annual Cost ($/kW)</th>
<th>Cost per Ton of Pollutant Removed ($/ton)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>&gt; 400</td>
<td>100 - 250</td>
<td>2 - 8</td>
<td>20 - 50</td>
<td>200 - 500</td>
</tr>
<tr>
<td></td>
<td>&lt; 400</td>
<td>250 - 1,500</td>
<td>8 - 20</td>
<td>50 - 200</td>
<td>500 - 5,000</td>
</tr>
<tr>
<td>Spray Dry</td>
<td>&gt; 200</td>
<td>40 - 150</td>
<td>4 - 10</td>
<td>20 -50</td>
<td>150 - 300</td>
</tr>
<tr>
<td></td>
<td>&lt; 200</td>
<td>150 - 1,500</td>
<td>10 - 300</td>
<td>50 - 500</td>
<td>500 - 4,000</td>
</tr>
</tbody>
</table>

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*a (EIA, 2002; EPA, 2000; Srivastava, 2001)

*b Assumes capacity factor > 80%
Advantages/Disadvantages

- Very high pollutant removal rate
- Easily obtained reagents
- Can be built without major retrofit
- High capital and running costs
- Messy
- High disposal costs
Hg
Mercury: The Next Big Step

- US EPA estimate: 45 t Hg emissions/year from coal electric plants.
- Average of 0.1 mg Hg/ton coal
- 60% of all Hg in coal is released to atmosphere
- Other pollution control devices can also capture mercury.
- Different installed control techs and conditions mean each plant must develop its own plan.

J. Air & Waste Manage. Assoc. 53:1318-1325
Current Hg Testing

- In coal: oxygen bomb/AA spectroscopy
  - ASTM D-3684 (up to 30% SD)
- In stack gases (direct measurement):
  - EPA 29, EPA 101A, Ontario Hydro Method, MESA
- Measurements are limited, difficult, long, and expensive.
- Continuous emissions monitoring (CEM):
  - Still in development, need validation, problems with interfering species.
EPA Method 7473

- Thermal decomposition, amagalmation, and AA spectroscopic analysis
- Normally used for water/soil.
- All solid byproducts of fuel burning and pollution controls can be measured.
- Use partial mass balance to calculate Hg emitted.
- 5 min/sample
- No sample prep.

Direct Mercury Analyzer
Milestone, Inc.
Validation of EPA 7473 with Coal

Low $\text{NO}_x$ Burner

----- vs. ----- 
Conventional Burner

Boylan, H.; R. Cain; H. M. Kingston.
*J. Air & Waste Manage. Assoc.*
53:1318-1325
# Hg Emission by Control Device

<table>
<thead>
<tr>
<th></th>
<th>Hg captured by sink</th>
<th>Hg emitted</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>FGD</strong></td>
<td>68% on FGD material</td>
<td>11% (11 kg/year)</td>
</tr>
<tr>
<td><strong>Low NO\textsubscript{x} burner and ESP</strong></td>
<td>43% on fly ash</td>
<td>57% (51 kg/year)</td>
</tr>
<tr>
<td><strong>ESP only</strong></td>
<td>1% on fly ash</td>
<td>99% (88 kg/year)</td>
</tr>
</tbody>
</table>
Mercury

- Chlorine present in coal will oxidize the mercury to Hg\(^{2+}\)
- Oxidized mercury can be removed more easily by scrubbers than elemental mercury
- Hg\(^{2+}\) is much more soluble in water than Hg\(^{0}\)
# Analysis of Power Plant Hg Capture

<table>
<thead>
<tr>
<th></th>
<th>CNS-P1</th>
<th>CNS-P2</th>
<th>CNS-P3</th>
<th>CNS-P5</th>
<th>CNS-P6</th>
<th>OH-LNB</th>
<th>EERC1</th>
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<tbody>
<tr>
<td><strong>Fuel</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl, daf wt %</td>
<td>0.128</td>
<td>0.174</td>
<td>0.135</td>
<td>0.156</td>
<td>0.151</td>
<td>0.091</td>
<td>0.0419</td>
</tr>
<tr>
<td>Hg, ppm</td>
<td>0.139</td>
<td>0.098</td>
<td>0.110</td>
<td>0.089</td>
<td>0.220</td>
<td>0.149</td>
<td>0.157</td>
</tr>
<tr>
<td><strong>Boiler</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rating, MW</td>
<td>290</td>
<td>193</td>
<td>180</td>
<td>–</td>
<td>1355</td>
<td>1338</td>
<td>1310</td>
</tr>
<tr>
<td>O₂, %</td>
<td>6.5</td>
<td>7.5</td>
<td>4.9</td>
<td>4.9</td>
<td>6.0</td>
<td>4.0</td>
<td>4.1</td>
</tr>
<tr>
<td><strong>FGD</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Type</td>
<td>MgLime</td>
<td>LS-F0</td>
<td>LS-N0</td>
<td>LS-N0</td>
<td>MgLime</td>
<td>MgLime</td>
<td>LS</td>
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<tr>
<td>ηSO₂, %</td>
<td>97</td>
<td>82</td>
<td>87</td>
<td>82</td>
<td>96</td>
<td>96</td>
<td>95</td>
</tr>
<tr>
<td>Slurry pH</td>
<td>6.5</td>
<td>6.1</td>
<td>5.8</td>
<td>5.8</td>
<td>6.5</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>L:G, gpm/acfm</td>
<td>60–75</td>
<td>94</td>
<td>73</td>
<td>50</td>
<td>30</td>
<td>30</td>
<td>–</td>
</tr>
<tr>
<td>IN[Hg, µg/dscm</td>
<td>8.2</td>
<td>6.5</td>
<td>10.6</td>
<td>6.8</td>
<td>17.9</td>
<td>9.1</td>
<td>8.2</td>
</tr>
<tr>
<td>IN[Hg₂⁺</td>
<td>0.736</td>
<td>0.797</td>
<td>0.874</td>
<td>0.703</td>
<td>0.707</td>
<td>0.872</td>
<td>0.572</td>
</tr>
<tr>
<td>OUT[Hg, µg/dscm</td>
<td>3.2</td>
<td>2.1</td>
<td>1.9</td>
<td>2.7</td>
<td>7.42</td>
<td>3.5</td>
<td>5.1</td>
</tr>
<tr>
<td>OUT[Hg₂⁺</td>
<td>0.159</td>
<td>0.124</td>
<td>0.150</td>
<td>0.382</td>
<td>0.162</td>
<td>0.370</td>
<td>0.198</td>
</tr>
<tr>
<td>ηHgCl₂, %</td>
<td>91.6</td>
<td>95.0</td>
<td>96.9</td>
<td>78.4</td>
<td>90.5</td>
<td>83.7</td>
<td>78.5</td>
</tr>
<tr>
<td>fSCRB, %</td>
<td>56.2</td>
<td>67.9</td>
<td>82.4</td>
<td>59.8</td>
<td>61.8</td>
<td>58.5</td>
<td>38.0</td>
</tr>
</tbody>
</table>

Recommendations

- Using pre-scrubbers to eliminate HCl is a bad idea. Less Hg is captured.
- HCl and O₂ levels along with FGD temp are most important in capturing Hg. No other factors correlate.
- Selective catalytic reduction (SCR) in combination with wet scrubber will eliminate most Hg, but more research must be done to make sure it is predictable. (Turkey)

Power Plant Pollution Controls

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3. Are pollution controls green?
Byproducts

- **Slag** – contains metal oxides, phosphorous, and ash. It can be used in concretes and fertilizers.

- **CFB ash** – good for blending with construction materials (gypsum). Very basic, so OK for landfills.

- **Slurry** – difficult to move and store before drying. Contains calcium sulfate.
Green?

■ Do pollution controls make fossil fuel-fired power plants green?
  ■ Pollution controls require large amounts of energy and reagents to run.
  ■ Combustor controls are better than flue gas controls.
  ■ Catalysts and easily recycled/cleaned asorbents should be preferred.