BCURA B73 Research Contract

“The Selection of Low Cost Sorbents & Process Conditions for Mercury Capture from Flue Gases”

Imperial College London
Department of Chemical Engineering
London SW7 2AZ

Prof D R Dugwell, Prof R Kandiyoti, Dr A George, Mr H R Seneviratne
MERCURY EMISSIONS REGULATIONS

- Mercury is a cumulative poison - causes kidney and brain damage

- USA – Clean Air Mercury Rule (CAMR)
  - cap & reduce mercury emissions from coal-fired power plants (2005)
    - 1st phase cap of 38 tpy effective in 2010
    - 2nd phase cap of 15 tpy effective in 2018

- Emission limits proposed by the US EPA (2005) – based on gross energy output
  - Bituminous units: 9.5 kg/TWh [had the highest limits]

- Canada Wide Standard
  - Bituminous units: 3 kg/TWh

- UK - No specific regulations yet for coal-fired power plants, however mercury emissions from the plants will be monitored
POSSIBLE COST EFFECTIVE METHOD OF MERCURY CAPTURE

- Based around current emission control systems
- Possible method
  - inject sorbent before particulate control device
PRINCIPAL ACTIVITIES

- Identification and sourcing of suitable sorbents
- Characterisation of promising sorbents
  - SEM
  - BET
  - TGA
- Hg retention capability
  - Adsorption temperature
  - flue gas composition [e.g. HCl and SO₂]
  - Hg speciation
- Measurement of leaching stability of Hg from spent sorbent
SORBENTS TESTED

- Commercial sorbents
  - Norit Darco Hg™
  - Norit Darco Hg-LH™

- Scrap tyre rubber
  - Tyre rubber charcoal
  - Tyre rubber activated carbon – steam activation
  - Tyre rubber activated carbon – Bromine impregnation

- Sewage sludge
  - Sewage sludge charcoal
  - Sewage sludge AC – bromine impregnation

- Coal fly ash – UK power plants (8 ashes)
MAKING SORBENTS FROM SCRAP TYRE & SEWAGE SLUDGE

- Char from scrap tyre pyrolysis
  - Pyrolysis temperature = 700°C

- Activated Carbon from scrap tyre
  - Activation temperature = 925°C

- Char from DEMAD sewage sludge
  - Pyrolysis temperature = 600°C

- Bromine impregnated activated carbon from scrap tyre rubber and sewage sludge
  - Pyrolysis temperature = 600°C

- Particle size between 38 – 75 μm
<table>
<thead>
<tr>
<th>Sorbent</th>
<th>BET surface area (m²/g)</th>
<th>Micropore volume (mm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit Darco Hg™</td>
<td>660</td>
<td>169</td>
</tr>
<tr>
<td>Norit Darco Hg-LH™</td>
<td>335</td>
<td>61</td>
</tr>
<tr>
<td>Fly ash</td>
<td>1 - 15</td>
<td>0.2 - 2</td>
</tr>
<tr>
<td>Tyre charcoal</td>
<td>76</td>
<td>1</td>
</tr>
<tr>
<td>Tyre AC -steam</td>
<td>249</td>
<td>67</td>
</tr>
<tr>
<td>Tyre AC -bromine</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>Sewage sludge charcoal</td>
<td>53</td>
<td>10</td>
</tr>
<tr>
<td>Sewage sludge AC -bromine</td>
<td>700</td>
<td>147</td>
</tr>
</tbody>
</table>
## ASH AND ELEMENTAL ANALYSIS

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>Ash</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>H</th>
<th>S</th>
<th>Cl</th>
<th>Br</th>
</tr>
</thead>
<tbody>
<tr>
<td>Norit Darco Hg™</td>
<td>10</td>
<td>77</td>
<td>0.6</td>
<td>4</td>
<td>0.2</td>
<td>0.4</td>
<td>0.03</td>
<td>&lt;100 ppm</td>
</tr>
<tr>
<td>Norit Darco Hg-LH™</td>
<td>27</td>
<td>58</td>
<td>0.4</td>
<td>6</td>
<td>0.3</td>
<td>1.1</td>
<td>0.03</td>
<td>3.05</td>
</tr>
<tr>
<td>Fly ash D</td>
<td>92</td>
<td>7</td>
<td>0.2</td>
<td>&lt;0.1</td>
<td>&lt;0.05</td>
<td>0.3</td>
<td>0.02</td>
<td>&lt;100 ppm</td>
</tr>
<tr>
<td>Tyre charcoal</td>
<td>13</td>
<td>83</td>
<td>0.3</td>
<td>&lt;0.1</td>
<td>0.3</td>
<td>3</td>
<td>0.03</td>
<td>510 ppm</td>
</tr>
<tr>
<td>Tyre AC – steam</td>
<td>13</td>
<td>83</td>
<td>0.4</td>
<td>&lt;0.1</td>
<td>0.1</td>
<td>3</td>
<td>0.01</td>
<td>NA&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>Tyre AC – bromine</td>
<td>4</td>
<td>90</td>
<td>0.3</td>
<td>3.0</td>
<td>0.2</td>
<td>0.8</td>
<td>0.01</td>
<td>1.08</td>
</tr>
<tr>
<td>Sewage sludge charcoal</td>
<td>71</td>
<td>23</td>
<td>2.5</td>
<td>&lt;0.1</td>
<td>0.7</td>
<td>1.0</td>
<td>0.06</td>
<td>0.01</td>
</tr>
<tr>
<td>Sewage sludge -bromine</td>
<td>32</td>
<td>47</td>
<td>4.6</td>
<td>7.8</td>
<td>0.9</td>
<td>1.9</td>
<td>0.01</td>
<td>2.09</td>
</tr>
</tbody>
</table>
- Inorganic species in fly ash agglomerated into spherical globules
- Wurtzite (ZnS) in sorbents from scrap tyre rubber – not part of the carbon matrix
- Bromine presence on the impregnated PAC confirmed
## SIMULATED FLUE GAS

### Harworth coal

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Concentration</th>
<th>Volume flow rate (at NTP) [ml/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg$^0$</td>
<td>3.5 ppm$_v$</td>
<td>1.3x10$^{-7}$</td>
</tr>
<tr>
<td>O$_2$</td>
<td>6%</td>
<td>2</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>12%</td>
<td>5</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>1800 ppm$_v$</td>
<td>7x10$^{-2}$</td>
</tr>
<tr>
<td>HCl</td>
<td>200 ppm$_v$</td>
<td>7x10$^{-3}$</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>7%</td>
<td>2.5</td>
</tr>
<tr>
<td>NO</td>
<td>490 ppm$_v$</td>
<td>2x10$^{-2}$</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>17 ppm$_v$</td>
<td>6x10$^{-4}$</td>
</tr>
<tr>
<td>N$_2$</td>
<td>75%</td>
<td>28 mL/min</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100%</strong></td>
<td><strong>37</strong></td>
</tr>
</tbody>
</table>
Test Temperature = 150 °C
Hg concentration = 29 ng/L
Experimental time = 60 min
Sorbent mass = 20 mg

Mercury vapor mixed with simulated flue gas

Flue gas to backup capture unit

Thermocouple Well

Electric Heater

Fixed Sorbent Bed

Kaowool Felt Disc
HG CAPTURE – TEMPERATURE

Gas scheme = Exp. 1

Mercury Capture Efficiency (%)

Test Temperature (Deg. C)

- Norit Darco Hg™
- Fly ash D
- Fly ash F
- Tyre char
- Tyre AC - steam

Sample mass = 100 mg  Hold time = 60 min
Sample mass = 100 mg
Norit Darco Hg™ - test duration = 60 min.  All other sorbents - test duration = 30 min.
HG CAPTURE – WITH SCHEME -1

Mercury Capture Efficiency (%)

Hold Time (minutes)

Note - sample mass = 100 mg        Test Temperature = 150°C
Note - Fly ash D was not tested with gas scheme Exp. 4
HG CAPTURE – EXP. 1 TO EXP. 6

Note - sample mass = 20 mg

Capture efficiency of Fly ash D calculated using expected 64ng input
HG CAPTURE – INITIAL EXPOSURE TO NO$_x$

- Sample mass = 100 mg
- Hold time = 60 min.
- Test temperature = 150°C
HG CAPTURE – INITIAL EXPOSURE TO HCL

Sample mass = 100 mg
Hold time = 60 min.

Test temperature = 150°C
THERMAL DESORPTION TESTS

Percentage of mercury that was desorbed
- Norit Darco Hg
- Tyre char
- Tyre AC - steam

Gas scheme Exp. 1: Grey, Gas scheme Exp. 2: Light blue, Gas scheme Exp. 3: Dark blue, Gas scheme Exp. 5: Black
Sample mass = 20 mg  Test Temperature = 150°C  Hold time = 60 min
BROMIDE IMPREGNATED PAC

Gas scheme = Exp. 6

Sample mass = 20 mg
Hold time = 60 min
Test Temperature = 150°C
FLY ASH FROM UK PLANTS

Mercury capture efficiency
- For mercury capture efficiency

Initial mercury concentration
- For initial mercury concentration

Mercury Capture Efficiency (%) vs. Loss on Ignition (LOI) (%)

Initial Hg concentration (ppm)

- Mercury capture efficiency
- For mercury capture efficiency

- Initial mercury concentration
- For initial mercury concentration
LEACHING TESTS – EXP. 1

US EPA – Safe Drinking Water Act = 2 ng/mL
LDR Limit = 25 ng/mL

Norit Darco Hg-LH
Tyre AC R3
Sewage sludge AC R3

Hg concentration in leachate (ng/mL)
Percentage of Hg leached from the sorbent (%)
LEACHING TESTS – EXP. 5

- Hg concentration in leachate
- Percentage of Hg leached from the sorbent

US EPA – Safe Drinking Water Act = 2 ng/mL
LDR Limit = 25 ng/mL

Norit Darco Hg
Norit Darco Hg-LH
Fly ash D
Fly ash E
Tyre char
Tyre AC - steam
Tyre AC - bromine
Sewage sludge char

Percentage of total Hg leached from the sorbent
CONCLUSIONS

- Brominated sorbents ~ 100% effective when gas scheme – Exp. 1 is used.
  - Needed less than 5% the mass of Norit Darco Hg™
- Sorbents without Br impregnation (except the fly ash)
  - Efficiency increased with NOX or HCl
- Tests with Exp. 1: Physically adsorbed - steam PAC
  Chemical bond – Tyre pyrolysis char
- Test with Exp. 5 – Strong chemical bond
  probably due to HCl
- Hg capture on fly ash related to LOI
  - LOI >17% needed to equal Br impregnated sorbents
- TCLP leaching test showed very little mercury is leached
  - Hg conc. in leachate < EPA safe limit for drinking water
CONCLUSIONS

- Norit Darco Hg™ substitute
  - Steam activated PAC from scrap tyre rubber

- Norit Darco Hg-LH™ substitute
  - Bromide impregnated PAC from scrap tyre rubber
RECOMMENDATIONS FOR FUTURE WORK

- Test with $\text{SO}_3$
  - Might consume active sites which would have adsorbed mercury

- Entrained flow reactor
  - Difficult to correlate bench scale fixed bed results with full-scale field tests
  - Entrained flow reactor results in USA have had better correlations with full-scale tests
Acknowledgment

I would like to express my sincere thanks to BCURA for funding this project and P S Analytical for providing the Mercury generator and helping in analysing the bromine impregnated sorbents.

Special thanks to the BCURA Project Officer, Dr D Fitzgerald, and also to Dr W. Quick and Dr S Weatherstone for their help and encouragement throughout the project.