CFD Modelling of Mercury Behaviour in Air-coal and Oxy-coal Combustion Systems

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Outline

- Introduction
- Objectives
- Gas-phase mechanism
- Gas-solid mechanism
- Results & discussion
- Conclusions
Introduction

Challenges associated with mercury studies

Experimental

Modelling
Mercury from coal
Chemistry

\[ \text{CO, CO}_2, \text{H}_2\text{O, H}_2, \text{N}_2, \text{O}_2, \text{NO}_x, \text{SO}_x \]

\[ \text{Cl, HCl, Cl}_2 \quad \text{HgCl, HgCl}_2 , \text{HgO} \]

\[ \text{Hg}^{2+} \]

\[ \text{Hg}^0 \]

\[ \text{O}_2 \quad + \]

Fly ash

\[ \text{Hg}^2+ \]

\[ \text{Hg}^p \]
About ~ 99% of the Hg in coal is evaporated as Hg\(^0\).

Coal (Hg content of ~1-100 ppm)

Less than 0.1% of the mercury in coal stays in bottom ash.

Hg\(^0\) is believed to be oxidized by the unburned carbon in fly ash (solid phase) and chlorinated compounds (gas phase).

Over 99% of the Hg\(^0\) is separated with the fly ash.

Hg\(^0\) leaves with the flue gases.

Most of Hg\(^2+\) is retained in the FGD sorbent or solution and leaves as waste or by product.
Objectives

- To study the effect of combustion conditions and other species on mercury transformation in air- and oxy-coal combustion.

- To develop, validate and optimize a reaction mechanism for mercury transformation applicable in coal combustion processes.

- This mechanism is implemented in Computational Fluid Dynamics (CFD) calculations.
Gas-phase reaction mechanism

Methodology

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**Reaction**

1. \( \text{Hg} + \text{Cl} + \text{M} = \text{HgCl} + \text{M} \)
2. \( \text{Hg} + \text{Cl}_2 = \text{HgCl} + \text{Cl} \)
3. \( \text{Hg} + \text{HCl} = \text{HgCl} + \text{H} \)
4. \( \text{Hg} + \text{HOCl} = \text{HgCl} + \text{OH} \)
5. \( \text{HgCl} + \text{Cl} + \text{M} = \text{HgCl}_2 + \text{M} \)
6. \( \text{HgCl} + \text{Cl}_2 = \text{HgCl}_2 + \text{Cl} \)
7. \( \text{HgCl} + \text{HCl} = \text{HgCl}_2 + \text{H} \)
8. \( \text{HgCl} + \text{HOCl} = \text{HgCl}_2 + \text{OH} \)

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Application of gas-phase mechanism in CFD - gas-phase only

- 3D geometry, ~15,000 hexahedral cells.
- Temperature imposed on the reactor wall and in the gas-phase by user-defined functions (UDFs).
- Reduced mechanism, 20 species and 51 gas-phase reactions.
- Rates defined in Arrhenius form and imported via CHEMKIN input file.
Mercury oxidation on carbon in ash is initialized by adsorption of gaseous mercury onto the surface, chlorination of the adsorbed mercury and its desorption to the gas phase.

\[
C_{(0)} + \text{Hg} \underset{k',k''}{\rightleftharpoons} C_{(Hg)} \\
C_{(Hg)} + \text{Cl} \xrightarrow{k''} C_{(HgCl)} \xrightarrow{k'''} C_{(0)} + \text{HgCl}
\]

Experimentally it has been shown that the adsorption and desorption isotherms often follow the trend of the Langmuir isotherm.\(^3\)

\[
r = k(\omega_{\text{max}} - \omega)[\text{Hg}] - k'\omega \quad \rightarrow \quad \omega = \omega_{\text{max}} \frac{(k/k')[\text{Hg}]}{1 + (k/k')[\text{Hg}]}
\]

\(k\) and \(k'\) calculated by using a regression approach.\(^3,4\)
Experimental setup
University of Kentucky

Details and configuration of the slipstream reactor (courtesy of University of Kentucky).

- Cross section: 0.152 x 0.152 m²
- Wall thickness: 0.01 m
- Insulated walls
- Temperature drop across the test area: 20 °C
- Sampling points: inlet, middle and outlet
- Ontario Hydro (OH) and Semi Continuous Emission Monitoring (SCEM) methods
- Results in reasonable agreement with experimental data

Coal analysis (Dry, %)

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>Cl (ppm)</th>
<th>Hg (ppm)</th>
<th>Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>72.9</td>
<td>5.0</td>
<td>10.0</td>
<td>1.0</td>
<td>1270</td>
<td>0.1</td>
<td>6.0</td>
</tr>
</tbody>
</table>
CFD case setup

- 2D geometry
- Reduced mechanism: 20 species and 51 gas-phase reactions
- Rates defined in Arrhenius form and imported via a CHEMKIN input file
- Gas-phase mechanism coupled to a heterogeneous mechanism
- User-defined functions (UDFs) to adjust the temperature on the reactor wall and in the gas-phase.
The inlet gas compositions for the oxy-coal combustion cases are calculated by using high temperature equilibrium calculations followed by a kinetic calculation to the inlet temperature.

Oxy once-through and wet recycled flue-gas combustion use a medium of 30/70 of O₂/CO₂.

<table>
<thead>
<tr>
<th>Flue gas composition (mole fraction at 623 K, %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
</tr>
<tr>
<td>-------</td>
</tr>
<tr>
<td>14.81</td>
</tr>
<tr>
<td>88.42</td>
</tr>
<tr>
<td>68.66</td>
</tr>
</tbody>
</table>

* once through oxy-coal condition, ** oxy-coal combustion with wet recycle
Coal chlorine results in ~100 ppm of gas-phase HCl, which contributes to less than 0.9% of mercury oxidation in the gas phase. This has been supported by experiments as well.5,6

The simulation in the presence of fly ash particles and mercury oxidation extent was found to increase by up to 2.5%.

Results and discussions

- Slight reduction in Hg oxidation for oxy-coal combustion conditions with once-through.
- Enhancement of oxidation for oxy-coal with wet recycle.
- ~0.13 ppm of mercury on the particles for [HCl] = 100ppm in both air- and oxy-coal conditions.
In addition to transformation in the gas phase, carbon content of the fly ash affects mercury speciation during coal combustion.

In this study, mercury oxidation on fly ash has been modelled using a commercial CFD code and Langmuir type reaction rates.

An improved prediction of mercury speciation for air- and oxy-coal combustion is achieved.

It is envisaged that by considering the variation of the heterogeneous properties of the particles and the gas-phase species during the oxy-coal combustion process, predictions can be improved.
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Thank you!

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