Influence of air combustion and oxy-fuel combustion flue gas constituents on Hg\(^0\) re-emission in WFGD systems

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INTRODUCTION: properties and toxicity of mercury

- High volatility
- High environmental persistence
- Bioacumulation
- Biomagnification

Mercury (Hg)

- CH$_3$Hg$^+$
- Kidsneys damage
- Nervous system alterations
- Cardiovascular diseases
- Fetus alterations

CH$_3$Hg$^+$ bioaccumulates and biomagnifies, leading to various toxic effects.
INTRODUCTION: sources of mercury

Natural sources

Anthropogenic sources

- Coal fired power plants and other combustion installations
- Production of chemicals
- Production and processing of metals
- Production of clinker cement or lime
- Mineral oil and gas refineries
- Others

INTRODUCTION: mercury behaviour in coal combustion systems

- **Boiler**
- **DeNOx**
- **Electrostatic precipitator**
- **Wet flue gas desulphurization** ("scrubber")

Chemical species:
- Hg\(^0\)
- Hg\(^{2+}\)
- Hg\(^p\)

Processes:
- Combustion in air
- Fly ash particles
- Gypsum
- Water

Diagram illustrates the flow of mercury and other species through the combustion and desulphurization processes.
INTRODUCTION: mercury behaviour in oxy-coal combustion systems

- Mercury species: Hg\textsubscript{0}, Hg\textsuperscript{2+}
- Oxy-coal combustion:
  - 70% CO\textsubscript{2}, 30% H\textsubscript{2}O
- Material failure of Al heat exchangers
- Air
- Oxygen (O\textsubscript{2} (> 95%))
- Criogenic separation
- ESP
- WFGD
- Compressor
- Gypsum
- Water
- Fly ash particles
- Mercury flue gas desulfurization (WFGD)
EXPERIMENTAL: laboratory scale system

- Water bath
- Evaporator
- N₂
- HOVACAL
- Peristatic pump
- Gas outlet
- Gas inlet
- Reactor
- pH Eh
- 50 µg·m⁻³ Hg²⁺
- Activated carbon
- Hg analyzer VM 3000
- Hg⁰ (g)
- Mercury solution
- N₂, O₂, CO₂
- Gypsum
- Hg²⁺ (g)
In a slurry containing: Gypsum (98%), limestone (2%) and sulphate ions,
Atmosphere: N\textsubscript{2}, H\textsubscript{2}O and HgCl\textsubscript{2} (Hg\textsuperscript{2+})
Mercury reduction might be caused by:

The presence of metal impurities derived from limestone (Fe, Mg...).

\[ 2\text{Me}^{2+}(aq) + \text{Hg}^{2+}(aq) \rightarrow \text{Hg}^0(g) + 2\text{Me}^{3+}(aq) \]

To ascertain whether the gas composition (oxy-combustion), can influence the mercury reduction process.
RESULTS: influence of O$_2$ concentration (N$_2$ balance)

$2\text{Me}^2+(\text{aq}) + \text{Hg}^2+(\text{aq}) \rightarrow \text{Hg}^0(\text{g}) + 2\text{Me}^3+(\text{aq})$

↑ Concentration of O$_2$  ↓ Re-emission of Hg$^0$  Hg slurry
RESULTS: influence of CO\textsubscript{2} concentration (N\textsubscript{2} balance)

![Graph showing the influence of CO\textsubscript{2} concentration on Hg emissions.]

- Concentration of CO\textsubscript{2}:
  - ↑

- Re-emission of Hg\textsuperscript{0}:
  - ↓

- Hg slurry:
  - ↓
RESULTS: influence of CO$_2$ concentration

\[
\begin{align*}
\text{Concentration of CO}_2 & \quad \uparrow \\
\text{Re-emission of Hg}^0 & \quad \downarrow \\
\text{pH} & \quad \downarrow \\
\end{align*}
\]
RESULTS: influence of CO$_2$ concentration (O$_2$ balance)

Re-emission of Hg$^0$ is affected by the pH and the concentration of O$_2$. 

- Decrease in pH decreases re-emission of Hg$^0$. 
- Increase in CO$_2$ percentage increases re-emission of Hg$^0$. 

[Hg$^0$] (µg m$^{-3}$) and pH vs. time (min) for different CO$_2$ concentrations:

- 0% CO$_2$: Hg$^0$ concentration decreases slowly over time.
- 20% CO$_2$: Hg$^0$ concentration decreases faster than 0% CO$_2$.
- 50% CO$_2$: Hg$^0$ concentration decreases faster than 20% CO$_2$.
- 70% CO$_2$: Hg$^0$ concentration decreases fastest among the concentrations tested.

Hg slurry
RESULTS: influence of flue gas composition

- Influence of pH on re-emission of Hg0:
  - $\approx 90$: $100$% CO2, $100$% O2
  - $\approx 20$: $90$% CO2, $10$% N2
  - $\approx 50$: $70$% CO2, $30$% N2
  - $\approx 25$: $70$% CO2, $30$% O2
  - $\approx 15$: $80$% CO2, $20$% N2

- Influence of O2 on pH:
  - $\approx 90$: $100$% CO2, $100$% O2
  - $\approx 20$: $90$% CO2, $10$% N2
  - $\approx 50$: $70$% CO2, $30$% N2
  - $\approx 25$: $70$% CO2, $30$% O2
  - $\approx 15$: $80$% CO2, $20$% N2
RESULTS: influence of H$_2$O concentration

High water vapor concentrations in the flue gas do not produce a significant effect on the re-emission of Hg
The effect of the CO$_2$, O$_2$ and water vapor on the reduction of Hg$^{2+}$ species by metallic impurities from limestone was determined.

- **High concentrations of O$_2$ in the flue gas prevent the re-emission of Hg$^0$ due to its destabilizing effect on the metals present in low oxidation states.**

- **High concentrations of CO$_2$, which cause a decrease in the pH of slurries reduce the amount of Hg$^0$ is re-emitted.**

→ The high concentrations of CO$_2$ in oxy-fuel combustion may help to decrease the amount of Hg$^0$ re-emitted.

→ The amount of metals present in limestone and the pH of slurries need to be strictly controlled to reduce Hg$^0$ re-emissions at power plants operating under oxy-fuel combustion conditions.
Thank you!

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