Semi-volatile heavy metals behavior during co-combustion of sludge and coal under $O_2/CO_2$ atmosphere

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Sewage sludge, as a solid waste, contains large amounts of toxic and hazardous substances, such as parasite, pathogen and heavy metals.

Fluidized-bed incineration is a promising technology to reduce the volume and the mass of sludge wastes.

Normally, sludge is combusted with coal because of the complex composition and unstable ignition characteristics.

Co-combustion of sludge and coal under O$_2$/CO$_2$ atmosphere could obtain dual benefits for sludge wastes treatment and CO$_2$ emission control.
As well known, the influences (such as fuel characteristics, operation condition, etc.) have significant effects on heavy metals migration during combustion.

However, the knowledge of heavy metals migration behavior during oxy-fuel combustion has not been well understood.

The objective of this study is to:

- Investigate the effect of reaction temperature, mass ratio of sludge to coal and atmosphere on heavy metals release.
- Particularly, four HMs (As, Cr, Ni, Pb)
Samples preparation:

◆ sludge
  ◆ Huai’an sewage treatment plant (Jiangsu, China)
  ◆ dried at 105°C for 8h
  ◆ particle size less than 150 μm

◆ coal
  ◆ Yulin bituminous coal (Shanxi Province, China)
  ◆ particle size less than 150 μm.
### Table 1. Proximate, ultimate analysis and lower heating value of tested sludge and coal

<table>
<thead>
<tr>
<th>Samples</th>
<th>Proximate Analysis, $W_t$ /%</th>
<th>Ultimate Analysis, $W_t$ /%</th>
<th>Q$_{net}$, MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V FC M A C H N S O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sludge</td>
<td>29.41 2.05 0.97 67.57 14.84 3.96 2.55 1.03 9.05</td>
<td></td>
<td>5.08</td>
</tr>
<tr>
<td>Coal</td>
<td>26.54 45.40 4.82 23.24 59.20 4.52 1.59 1.54 5.09</td>
<td></td>
<td>22.10</td>
</tr>
</tbody>
</table>

### Table 2. Analyses of minor metals and heavy metals of samples (air dry basis)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Minor metals (wt%)</th>
<th>Heavy metals (mg·kg$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P Cl Si Al Fe K Ca Na Mg</td>
<td>As Cr Ni Pb</td>
</tr>
<tr>
<td>sludge</td>
<td>0.95 0.29 14.96 5.59 2.66 2.00 4.16 0.75 0.96</td>
<td>105.9 94.7 85.4 84.67</td>
</tr>
<tr>
<td>coal</td>
<td>0.02 0.07 5.73 2.01 0.61 0.23 0.58 0.02 0.08</td>
<td>31.75 22.73 2.39 44.56</td>
</tr>
</tbody>
</table>
Experimental condition

- Sample load: 5 g
- Mass ratio of sludge to coal ($X_s$): 0.25, 0.50 and 0.75
- Atmosphere: air (21%O₂/79%N₂)
  $$\text{CO}_2/\text{O}_2 \text{ with the variation of O}_2 = 21\%-50\%$$
- Reaction temperature $T_r$: 700-1000 ºC
- Residence time ($\tau$) for co-combustion: 20 min
Sample digestion and analysis

- All samples (including dried sludge, coal, the slag after co-combustion were digested in a PTFE beaker with an acid mixture (HF, HCl, HClO₄ and HNO₃)
- ICP-AES (inductively coupled plasma atomic emission spectrometry)

Calculation of release fraction

The release fraction of each target heavy metal was determined by following equation:

$$R = (1 - \frac{C_2 \times m_2}{C_1 \times m_1}) \times 100\%$$
Simulation condition

- Software: HSC-Chemistry 7.0
- Pressure: $P = 1.013 \times 10^5 \text{Pa}$
- Atmosphere: air (21%O$_2$/79%N$_2$) 
  
  $\text{CO}_2/\text{O}_2$ with the variation of $\text{O}_2 = 21\% - 50\%$
- Reaction temperature $T_r$: 700-1000 °C
- Considered elements: C, H, O, N, S
  
  Minor metals (P, Cl, Si, Al, Fe, K, Ca, Na, Mg)
  Heavy metals (As, Cr, Ni, Pb)
Results and discussion

Effect of reaction temperature on the release fraction of heavy metals

- Release fractions of As and Pb increase with increasing reaction temperature.
- Reaction temperature had little influence on the release of Ni and Cr.
- The order of release fraction was Pb > As > Ni > Cr.

- Higher SiO₂, CaO and Al₂O₃ existed in the sludge.
- Formed complex minerals (NiO·Al₂O₃, CaO·Cr₂O₃).
- Result in solidification of Ni and Cr.
Results and discussion

Effect of mass ratio on the release fraction of heavy metals

- Higher moisture existed in the tested coal
- Formed $\text{CrO}_2(\text{OH})_2(g)$
  
  
  $$0.5\text{Cr}_2\text{O}_3(\text{s}) + 0.75\text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) = \text{CrO}_2(\text{OH})_2(\text{g})$$

- Result in more emission of Cr

HMs migration during co-combustion with certain mass ratio cannot be predicted by the behavior during mono-combustion of sludge and coal.
Results and discussion

◆ Effect of mass ratio on the release fraction of heavy metals

- HMs migration during co-combustion with certain mass ratio cannot be predicted by the behavior during mono-combustion of sludge and coal.

- Higher Cl existed in the tested sludge

- The simulation result suggested the formation of \( \text{PbCl}_4(\text{g}) \) and \( \text{PbCl}_2(\text{g}) \) was promoted

- Result in more emission of Pb

- \( T_r = 900^\circ\text{C}; 30\%\text{O}_2/70\%\text{CO}_2 \)
Results and discussion

Effect of O₂ concentration on the release fraction of heavy metals

The simulation results suggested

- Higher O₂ concentration may promote the formation of PbCl₄(g) and CrO₂(OH)₂(g)
- Higher O₂ concentration may limit the formation of AsO(g) and AsO₂(g)

- Release fraction of Cr, Ni and Pb exhibited a similar variation tendency, and increased with increasing O₂ concentration.

- Opposite tendency was observed for As release.
Results and discussion

* Difference between O₂/N₂ and O₂/CO₂ on the release fraction of heavy metals

- The particle temperature decreased when replacing the N₂ with CO₂
- The boundary layer diffusion of oxygen to the particles is slower in CO₂
- CO₂ in the boundary layer stores more energy due to higher heat capacity
- Result in less emission of Cr and Pb

The difference of release fraction of Cr and Pb was observed between O₂/N₂ and O₂/CO₂
Conclusions

- Reaction temperature promotes the release of As and Pb significantly and has little influence on the release of Cr and Ni.

- Release fractions of As and Pb increase with increasing mass ratio of sludge to coal.

- Release fractions of Cr, Ni and Pb increase with increasing O₂ concentration.

- Oxy-combustion is helpful for solidification of As.

- O₂/CO₂ is helpful for control the emission of Cr and Pb.
Thank you for your attention!