Effects of pressure and CO concentration on petcoke mineral transformations for slag viscosity correlation development

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Knowledge of oxidation states of transition elements is critical in slag viscosity correlation development.

- Fuels mostly used: coal, pet coke\textsuperscript{a,b}.
- Significant V, Fe and Ni oxides in pet coke ash\textsuperscript{c}.

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\textsuperscript{a}Higman & Burgt, 2008; \textsuperscript{b}Murthy et al., 2014; \textsuperscript{c}Bennett et al., 2011; \textsuperscript{d}IGCC power plant, Veolia Water Technologies - Puertollano, Spain; \textsuperscript{e}Vargas et al., 2001

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\begin{itemize}
\item A gasification plant\textsuperscript{d}
\item Schematic of an entrained flow gasifier\textsuperscript{c}
\item Slag flow along hot-face of refractory\textsuperscript{c}
\end{itemize}

Slag can be considered as a network of tetrahedral SiO\textsubscript{2} units (Si: big circles; O: small circles). Cations could enter that space and modify the network structure and viscosity\textsuperscript{e}.
Viscosity correlations not available for petcoke ash slag

- Existing coal ash slag viscosity models: Urbain models⁴,⁵,⁶
- Combustion of petroleum coke: reduced rate of oxidation and excess carbon in fly ash can inhibit formation of corrosive $V_2O_5$⁷,⁸
- Coal-petcoke combustion: no $V$ or Ni phases⁹,¹⁰
  - Petcoke ash and slag experiments in oxidizing and reducing environment:
    - Petcoke combustion ash from CFBC (circulating fluidized bed combustion) boiler– $Ca_2V_2O_7.2H_2O$, $Na_4V_2O_7.18H_2O$¹¹
    - Reducing & oxidizing environment - $V_2O_3$ addition caused changes in AFT (ash fusion temperature); $V_2O_3$ and Fe$V_2O_4$ in reducing environment increased AFT and $Ca_2V_2O_7$ in oxidizing environment decreased AFT¹²
    - Effect of CaO, Fe₂O₃, NiO – high melting Ni$_2$SiO$_4$ and low melting $Ca_2V_2O_7$ affect AFTs¹³
    - $V$ volatility behavior studied during gasification - $V_2O_3$ & Fe$V_2O_4$ found in CO₂ gasified petcoke ashes (1100-1500 °C)¹⁴
    - Volatility of V & Ni studied in steam gasification of petcoke & biomass - $V_2O_3$, Fe$V_2O_4$, Ni, NiS in gasification ashes¹⁵
    - Petcoke ash experiments with 60% CO (rest CO₂) - $V_2O_3$ and Fe$V_2O_4$ (high melting point) in quenched slag increase AFT; upon coal & CaO addition Ca$3Fe_2Si_3O_{12}$ & Ca$3V_2O_8$ (low melting phases) decrease AFT¹⁶
    - Ca$_3$SiO$_4$, V$_2$O$_3$ and Fe$V_2O_4$ in petcoke ash resulted in high AFTs; appearance of low melting point calcium vanadium oxide and KAlSi$_2$O$_6$ and reduction in V$_2O_3$ on biomass addition to petcoke ash decreased AFT¹⁷
    - Coal-petcoke quenched slag formed in 64% CO (rest CO₂) had V$_2O_3$ in high petcoke mixtures¹⁸
    - XRD on coal-petcoke ash mixtures heated and quenched – V$_2O_3$, VFe$_2O_4$¹⁹
    - Coal ash with V and Ni – quenched slag had V$_2O_3$, Ni, CaAl$_2$Si$_2$O$_8$²⁰
- Hot stage XRD:
  - phases identified for coal and biomass (co-combustion) ash during heating (up to 1250 °C) and cooling cycles explained viscosity w.r.t. temperature²¹
  - phases identified for coal ash slag under reducing environment²²

*Hurst et al., 1999;¹ Uribain et al., 1981;² Kalmanovitch et al.;³ Bryers, 1996;⁴ Bryers, 1995;⁵ Srikanth et al., 2003;⁶ Wu et al., 2011;⁷ Jia et al., 2002;⁸ Li et al., 2017;⁹ Li et al., 2018;¹⁰ Xiong et al., 2018;¹¹ Srikanth et al., 2003;¹² Nakano et al. 2011;¹³ Nakano et al., 2009;¹⁴ Arvelakis et al., 2006;¹⁵ Schimpke et al., 2017.
Research objectives

• Effect of reducing gas (CO) and pressure on petcoke ash transformations

• Establish slag correlation development by linear regression
Experimental techniques used

High pressure thermogravimetric analyzer (HP TGA): $P$ up to 40 bar, $T$ up to 1260 °C.

X-Ray Diffractometer (XRD) with chamber for reducing gas: $T$ up to 1260 °C.
Superimposition of mass loss curves of $V_2O_5$, NiO and Fe$_2$O$_3$ on synthetic petcoke ash shows that the mass loss in synthetic petcoke ash is mainly due to reduction of $V_2O_5$, NiO and Fe$_2$O$_3$.

- **TGA results:** 1.01 bar, 70 % CO – 30 % CO$_2$

- **Increment in mass of Fe$_2$O$_3$ and $V_2O_5$ after 800 °C – formation of some phases**

<table>
<thead>
<tr>
<th>Component</th>
<th>(%)</th>
</tr>
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<tbody>
<tr>
<td>BaO</td>
<td>0.087</td>
</tr>
<tr>
<td>SrO</td>
<td>0.043</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>10.001</td>
</tr>
<tr>
<td>CaO</td>
<td>4.022</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>8.697</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>1.848</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>10.219</td>
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<tr>
<td>MnO</td>
<td>0.076</td>
</tr>
<tr>
<td>MgO</td>
<td>0.326</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>1.631</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.652</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.435</td>
</tr>
<tr>
<td>$V_2O_5$</td>
<td>48.266</td>
</tr>
<tr>
<td>NiO</td>
<td>13.697</td>
</tr>
<tr>
<td>Total</td>
<td>100.000</td>
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</tbody>
</table>

Synthetic petcoke ash composition
Increase in pressure causes reduction reactions to occur at higher temperatures

- High pressure TGA runs showed that the reduction reactions occur at higher temperatures

- Phase formations cause mass gain till 1000 °C (confirmed by equilibrium calculations in FactSage)
$V_2O_5$ and NiO peaks disappear by 650 °C in 70% CO indicating complete reduction of both $V_2O_5$ and NiO.

- Atmospheric pressure TGA run: mass loss calculations show that $V_2O_5$ can transform to $V_2O_3$ in the reducing environment.

- XRD: $V_2O_5$ and NiO peaks disappear by 657.8 °C. Sample consisted of SiO$_2$-Al$_2$O$_3$-CaO-Fe$_2$O$_3$-$V_2O_5$-NiO.
CO-CO$_2$ mixtures (as low as 10% CO) showed complete reduction of V$_2$O$_5$ by 750 °C. Higher CO content causes faster reduction of V$_2$O$_5$ w.r.t. temperature.

A: V$_2$O$_5$; B: Ca$_4$(Al$_8$Si$_8$O$_{32}$)(H$_2$O)$_{18.664}$; C: NiO; D: Fe$_2$O$_3$; E: Fe$_2$O$_3$; F: SiO$_2$; G: AlO(OH)
A generic viscosity correlation was developed for blends of coal - petcoke ash slag based on the work of Wang et al.\textsuperscript{a} and Hurst et al.\textsuperscript{b}

\[
\ln(\eta) = \ln(A) + \ln(T) + \frac{B}{RT}
\]

\[
x = \frac{m_s}{m_s + m_a + m_c + m_f}, \quad y = \frac{m_c + m_f}{m_a + m_c + m_f}
\]

\[
\ln(\eta) = a_0 + a_1y + a_2y^2 + a_3x + a_4xy + a_5xy^2 + a_6x^2 + a_7x^2y + a_8x^2y^2 + a_9x^3 + a_{10}x^3y + a_{11}x^3y^2
\]

Evaluate \(a_0 - a_{11}\) at \(1450^\circ C\) and \(1500^\circ C\)

A and B for a slag composition

\textbullet\ Viscosity data of petcoke ash slag from literature used to develop correlation\textsuperscript{a}

<table>
<thead>
<tr>
<th>\text{CC}\textsuperscript{a}</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>45.18</td>
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<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>29.99</td>
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<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
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<tr>
<td>CaO</td>
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<tr>
<td>MgO</td>
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<tr>
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<tr>
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<td>1.64</td>
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<td>K\textsubscript{2}O</td>
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<tr>
<td>Na\textsubscript{2}O</td>
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<tr>
<td>P\textsubscript{2}O\textsubscript{5}</td>
<td>0.29</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
</tr>
</tbody>
</table>

\textbullet\ \(V_2O_3\) and NiO added to baseline coal composition (CC)

\textbullet\ Compositions normalized to SiO\textsubscript{2} - Al\textsubscript{2}O\textsubscript{3} - CaO - FeO - \(V_2O_3\) - NiO
Model predictions show reasonable agreement with available viscosity data up to 7.5 % \( \text{V}_2\text{O}_5 \) and NiO each and in 60% CO atmosphere (rest being CO\(_2\)).

\[ \text{\textsuperscript{a}Wang \ et \ al., \ 2014} \]
Path forward....

Based on these results, viscosity correlations will be developed for pet coke compositions with higher proportions of V and Ni oxides.
Conclusions

• Gasifier’s reducing environment clearly reduces \( V_2O_5 \) at or below 750 °C
• At higher pressures experienced in industrial gasifiers the reduction occurs at higher temperatures
• This study clearly demonstrated that the phases to be used in correlating slag viscosity with chemical composition for V, Ni and Fe should be \( V_2O_3 \), NiO and FeO.
Thank you

Danke Shon!

Questions?
References


R. W. Bryers, "Fireside slagging, fouling, and high-temperature corrosion of heat-transfer surface due to impurities in steam-raising fuels." Progress in energy and combustion science 22, no. 1, pp. 29-120, 1996.


