Effect of Vanadium and Nickel Oxides on Petcoke Ash/Slag Viscosity Under Gasification Conditions

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Presentation outline

- Introduction
- Differences between Pet coke and coal
  - Inadequacies in predictive capabilities
- Research objectives of this study
- Experimental setup and samples used
- Influence of Ni and V on the slag viscosity
- Interaction mechanisms
- Some conclusions and future direction
Analysis of USDOE and other project reports indicated over 300 issues that needed to be solved for reliable operation.

"Reliance Industries' Jamnagar project...is one of the world's largest gasification projects, processing 9.8 million t/a petroleum coke from the adjacent Reliance refineries."

Power Magazine
Gasification of coal is growing in developing countries for chemicals

Gasifiers operational experience shows issues with availability.

IGCC availability is therefore, the most important technical issue governing the success or failure of these plants.

Source: Barnes, Ian, Recent operating experience and improvement of commercial IGCC, IEA report 113/10, 2013.
Petroleum coke as gasification feedstock is increasing

• The amount of petroleum coke, a by-product of the oil refining industry, has been increasing and is expected to continue to increase.

• Due to low reactivity, high gasification temperature is required. Entrained-flow gasification at high temperature and high pressure is more suitable for petroleum coke gasification.

• Ash of petroleum coke is mainly composed of vanadium and nickel.
Petcoke availability

Petroleum coke, gross inland availability (thousand metric tons)
Top 10 countries for the latest values

Composition of slag from coal and petcoke from entrained flow gasifier (Texaco) are different

<table>
<thead>
<tr>
<th></th>
<th>Coal</th>
<th>Petcoke</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Eastern</td>
<td>Western</td>
</tr>
<tr>
<td>SiO2</td>
<td>52.1</td>
<td>42.0</td>
</tr>
<tr>
<td>Al2O3</td>
<td>15.4</td>
<td>25.0</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>7.3</td>
<td>20.9</td>
</tr>
<tr>
<td>CaO</td>
<td>17.4</td>
<td>9.5</td>
</tr>
<tr>
<td>MgO</td>
<td>3.7</td>
<td>--</td>
</tr>
<tr>
<td>NiO</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>V2O5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Others</td>
<td>4.1</td>
<td>2.6</td>
</tr>
<tr>
<td>Carbon%</td>
<td>9.5</td>
<td>9.7</td>
</tr>
</tbody>
</table>

**Ash Fusibility, °F**

<table>
<thead>
<tr>
<th></th>
<th>ID</th>
<th>ST</th>
<th>FT</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>2120</td>
<td>2150</td>
<td>2250</td>
</tr>
<tr>
<td>ST</td>
<td>2140</td>
<td>2210</td>
<td>2430</td>
</tr>
<tr>
<td>FT</td>
<td>--</td>
<td>--</td>
<td>&gt;2700</td>
</tr>
</tbody>
</table>

Rheological properties of pet coke slag need to be studied

High viscosity – Difficult to remove
Low viscosity- Refractory corrosion
Operating conditions need to be selected for optimum viscosity

Models for prediction of viscosity of coal slag are well developed. However, methods to predict viscosity of pet coke slag need development.

FactSage is also not an adequate tool for this as Vanadium compounds not present in the solution database. It predicted more solid phase than actually present.

Source: Marc A. Duchesne et al., Flow behaviour of slags from coal and petroleum coke blends
• Several methods of estimating or measuring the critical viscosity temperature of molten coal ash slags have been developed over time:

  • Empirical modeling based on ash cone fusion temperatures,
  • Direct measurement of slag viscosity as a function of temperature, and
  • Thermophysical modeling based on coal ash composition
Slag formation and ash fusion temperatures

- The AFT results only indicated the initial deformation temperature (IDT) at 1300 °C, whereas slag formation already started to take place from 1000 °C.
- An AFT analyses only supplies information on the temperature where a mass of material, enough to deform the structure of the cone, starts to slag.
- The AFT also gives no information on the properties of the slag below that point.

Recent study of synthetic slags did not show a good correlation between ST and Tcv. USGS COALQUAL database identifiers and compositions (% mass/mass) of synthetic coal ashes used in this study. Sample 7 is not a part of the USGS COALQUAL database; it is included in this study to expand the composition range to include slags with lower iron(III) oxide content.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>COALQUAL identifier</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W236240</td>
<td>40.8</td>
<td>20.4</td>
<td>0.6</td>
<td>0.8</td>
<td>0.35</td>
<td>2.45</td>
<td>0.8</td>
<td>32.6</td>
</tr>
<tr>
<td>2</td>
<td>W201717</td>
<td>38.1</td>
<td>25.4</td>
<td>2.6</td>
<td>0.7</td>
<td>0.3</td>
<td>1.6</td>
<td>1.0</td>
<td>27.5</td>
</tr>
<tr>
<td>3</td>
<td>WAVE 2</td>
<td>36.7</td>
<td>29.3</td>
<td>0.9</td>
<td>0.3</td>
<td>0.1</td>
<td>0.7</td>
<td>0.7</td>
<td>31.4</td>
</tr>
<tr>
<td>4</td>
<td>W233566</td>
<td>35.7</td>
<td>20.4</td>
<td>2.0</td>
<td>0.5</td>
<td>0.2</td>
<td>1.6</td>
<td>0.9</td>
<td>36.7</td>
</tr>
<tr>
<td>5</td>
<td>W188929</td>
<td>44.8</td>
<td>24.0</td>
<td>1.0</td>
<td>0.6</td>
<td>0.1</td>
<td>1.5</td>
<td>1.0</td>
<td>27.1</td>
</tr>
<tr>
<td>6</td>
<td>W216040</td>
<td>45.1</td>
<td>20.5</td>
<td>1.1</td>
<td>0.7</td>
<td>0.1</td>
<td>2.5</td>
<td>1.3</td>
<td>28.7</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>49.6</td>
<td>26.3</td>
<td>2.1</td>
<td>1.1</td>
<td>0.64</td>
<td>2.4</td>
<td>1.2</td>
<td>15.4</td>
</tr>
</tbody>
</table>

- Correlation between ST and HT with Tcv was found to be poor, with $R^2$ values between 0.04 and 0.06. We observed a positive linear correlation between FT and Tcv, with a $R^2$ value of 0.77.
- They also found that it was possible to fit a plane to the Tcv data, using the silica-to-alumina ratio (S/A) and the iron(III) oxide equivalent (F) as independent variables ($R^2 = 0.96$).

Kalmanovitch or Modified Urbain Equation

Calculation Procedure

Step 1: Determine the mole fraction of all components based on the chemical oxide composition. Fe₂O₃ is converted to equivalent FeO.

Step 2: Calculate $M$ where

$$M = \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{FeO} + 2\text{TiO}_2$$

mole fractions

Step 3: Calculate $\alpha$ where

$$\alpha = \frac{M}{(M + \text{Al}_2\text{O}_3)}$$

mole fractions

Step 4: Calculate $B$ where

$$B = \text{BO} + (B1^*\text{SiO}_2) + (B2^*(\text{SiO}_2)^2) + B3^*\text{SiO}_3$$

$$\text{BO} = 13.8 + 39.9355^*\alpha - 44.049^*(\alpha^2)$$

$$B1 = 30.481 - 117.1505^*\alpha + 129.9978^*(\alpha^2)$$

$$B2 = -40.9429 + 234.0486^*\alpha - 300.04^*(\alpha^2)$$

$$B3 = 60.7619 - 153.9276^*\alpha + 211.1616^*(\alpha^2)$$

Step 5: $\ln[A] = -(0.2812^*B + 11.8279)$.

Step 6: Calculate the natural log of the viscosity at a given temperature $T$ in degrees K.

$$\ln[\text{viscosity}] = \ln[A] + \ln[T] + (1000^*B/T)$$

Plastic Viscosity (Einstein-Roscoe equation)

- The effective viscosity ($\eta$) of a molten silicate containing a suspension of solid crystals has been described for magmas and slags Einstein-Roscoe equation:

\[
\eta = \eta_0 (1-R\Phi)^{-2.5}
\]

- where
- $\eta_0$ is the fluid viscosity in the absence of solids,
- $\Phi$ is the solid volume fraction, and
- $R$ is the inverse of the maximum solid volume fraction (i.e. $R = \Phi^{-1}$).

Research Objectives

• To understand the effect of vanadium and nickel oxides on Petcoke slag viscosity

• To modify existing empirical correlations such as the Modified Urbain equation for prediction of viscosity of Petcoke slag.
Systematic variation of V and Ni based oxides using synthetic ash performed

- Effect of V oxides
  - 3 runs with increasing V$_2$O$_5$ content, without NiO

- Effect of interaction between V and Ni oxides
  - Effect of V$_2$O$_3$
    - 3 runs with increasing V$_2$O$_3$ conversion. Containing both V$_2$O$_5$ and NiO

- Effect of Ni oxides
  - 3 runs with increasing NiO content, without V$_2$O$_5$

A baseline without any V or Ni oxides, containing other oxides in the same ratio was also used
**Composition of slag samples used in the study**

Baseline

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>TiO₂</th>
<th>K₂O</th>
<th>MgO</th>
<th>Na₂O</th>
<th>SrO</th>
<th>BaO</th>
<th>MnO</th>
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<tr>
<td>48.07</td>
<td>19.73</td>
<td>14.60</td>
<td>4.867</td>
<td>1.867</td>
<td>5.867</td>
<td>1.467</td>
<td>3.733</td>
<td>1.467</td>
<td>0.267</td>
<td>0.067</td>
</tr>
</tbody>
</table>

**Ratios studied**

<table>
<thead>
<tr>
<th>V₂O₅</th>
<th>NiO</th>
<th>V₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>35</td>
<td>0</td>
</tr>
<tr>
<td>35</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td>25</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>0</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8.75</td>
<td>26.2</td>
<td>0</td>
</tr>
<tr>
<td>17.5</td>
<td>17.5</td>
<td>0</td>
</tr>
<tr>
<td>26.2</td>
<td>8.75</td>
<td>0</td>
</tr>
<tr>
<td>24.9</td>
<td>8.75</td>
<td>1.30</td>
</tr>
<tr>
<td>21</td>
<td>8.75</td>
<td>5.25</td>
</tr>
<tr>
<td>13.1</td>
<td>8.75</td>
<td>13.1</td>
</tr>
</tbody>
</table>
Several parameters that affect slag viscosity were considered.

- Gaseous atmosphere
- Chemical composition (Ni, V content)
- Temperature
- Number of crystals
- Size of crystals
- Oxidation state of phases
Methodology used for measurement of slag viscosity

Synthetic ash Preparation → Compact slag preparation → Grinding of slag → Viscosity Measurement

Theta HT - Rotating Viscometer Specifications
- Maximum furnace temperature = 1600 °C
- Viscosity range possible = 100 - 4 x 10^7 cP
- Any gaseous atmosphere or under vacuum

Example of measurement data
Steps involved in the measurement of slag viscosity

- **Loading slag sample into crucible**
  - **Room Temperature**

- **Insert rotor into liquid**
  - **1550 °C**

- **Homogenization**
  - **1550 °C - 60 mins**

- **Measurement**
  - **1550 °C to 1300 °C**

- **Remove rotor**
  - **1550 °C**

- **Drain liquid from rotor**
  - **1550 °C - 25 mins**

- **Cool**
  - **Room temperature**

**CO-CO2 mixture inserted into system after purging**

- **Around 1000 °C**

**Figure:** Diagram of the experimental setup with labeled components such as gas inlet, water inlet, viscometer control, power control, viscometer, water outlet, gas outlet, alumina radiation shields and supports, alumina crucible and spindle, and vacuum pump, with a furnace at the center and a process flowchart indicating the sequence of steps.
Reproducibility of the measurements was satisfactory.
$V_2O_5$ and NiO increase slag viscosity
Changes in crystalline Ni and V phases

- NaCaAl(SiO₇)
- NiFeO₄
- FeV₂O₄
- Ni(V₂O₆)
- Fe₃O₄/FeV₂O₄
- NiFeO₄
- Magnetite
- Spinel
- NiO
- Fe₂O₃
- FeO
- V₂O₃
- VFeO₃/Fe₂O₃
- VFeO₃/V₂O₃/Fe₂O₃
- VFeO₃/V₂O₃/FeO₃
SEM-EDX supports the formation of V-Fe compounds at high V2O5 contents.
SEM-EDX supports the formation of Ni-Fe compounds at high NiO contents
SEM-EDX supports the interaction between V and Ni phases

V17.5Ni17.5
Image analysis shows fewer larger crystals as V content increases.

<table>
<thead>
<tr>
<th>V</th>
<th>Ni</th>
<th>Crystal count</th>
<th>Average crystal size</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>0</td>
<td>1893</td>
<td>43</td>
</tr>
<tr>
<td>26.5</td>
<td>8.75</td>
<td>971</td>
<td>153</td>
</tr>
<tr>
<td>17.5</td>
<td>17.5</td>
<td>3667</td>
<td>29</td>
</tr>
<tr>
<td>8.75</td>
<td>26.5</td>
<td>3776</td>
<td>35</td>
</tr>
<tr>
<td>0</td>
<td>35</td>
<td>3689</td>
<td>18</td>
</tr>
</tbody>
</table>
Combination of oxidation state of phases, number and size of crystals determines viscosity

Viscosity increases with higher V content since-
- $V_2O_5 \rightarrow Ni(V_2O_6) \rightarrow V_2O_3 \rightarrow FeV_2O_4 \rightarrow VFeO_3$
- $Fe_3O_4 \rightarrow Fe_2O_3$
- Increase in crystal size in spite of decrease in number

Viscosity increases with higher Ni content since-
- Number of crystals increases although they are smaller
Effect of addition of vanadium and nickel

T250 value increased with increasing Ni and V content

\[ y = 3.6486x + 1284.6 \]
\[ R^2 = 0.8509 \]

\[ y = 4.9368x + 1287.8 \]
\[ R^2 = 0.9984 \]
Experimental data was fitted to obtain the effect of V and Ni content individually.

\[ y = 0.1983x^2 + 2.108x + 17.334 \]
\[ R^2 = 1 \]

\[ y = 0.7462x^2 - 0.949x + 17.334 \]
\[ R^2 = 1 \]
Interaction between Ni and V phases led to a viscosity higher than predicted based on individual effects.

<table>
<thead>
<tr>
<th>$V_2O_3$</th>
<th>$V_2O_5$</th>
<th>Ni</th>
<th>Measured Viscosity</th>
<th>Calculated values</th>
<th>Ratio of measured to calculated viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>17.33</td>
<td>17.33</td>
<td>1.0</td>
</tr>
<tr>
<td>0</td>
<td>15</td>
<td>0</td>
<td>93.58</td>
<td>93.57</td>
<td>1.0</td>
</tr>
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<td>0</td>
<td>25</td>
<td>0</td>
<td>194</td>
<td>194</td>
<td>1.0</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>17.33</td>
<td>17.33</td>
<td>1.0</td>
</tr>
<tr>
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<td>15</td>
<td>171</td>
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<td>1.0</td>
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<tr>
<td>0</td>
<td>0</td>
<td>25</td>
<td>460</td>
<td>460</td>
<td>1.0</td>
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<tr>
<td>0</td>
<td>17.5</td>
<td>17.5</td>
<td>1280</td>
<td>344.20</td>
<td>3.72</td>
</tr>
<tr>
<td>0</td>
<td>26</td>
<td>8</td>
<td>400</td>
<td>263.69</td>
<td>1.51</td>
</tr>
</tbody>
</table>

Park and Oh studied the viscosity of Korean anthracite slag, which contains a large portion of vanadium trioxide ($V_2O_3$). They observed that, in order to keep the slag flowing, the temperature had to be kept above 1,670 °C, which is 270 °C above the typical operating temperature for slurry-feed gasifiers.

Conversion to V2O3 increases viscosity before a decrease.

- **5% conversion to V2O3**: Viscosity increases initially, then decreases.
- **20% conversion to V2O3**: Similar pattern as 5% conversion.
- **50% conversion to V2O3**: Viscosity increases again.

**Materials Composition**:
- V2O5: 26.25%
- NiO: 8.75%
$V_2O_3$ increases viscosity up to a certain concentration with higher number of crystals.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|c|c|}
\hline
V2O3 & V2O5 & Ni & Crystal count & Avg. crystal size & T250 (°C) \\
\hline
1.3 & 24 & 8.75 & 2745 & 48.6 & 1404 \\
5.25 & 21 & 8.75 & 4802 & 55.6 & 1427 \\
13.1 & 13.1 & 8.75 & 2072 & 59.2 & 1414 \\
\hline
\end{tabular}
\end{table}
Covalent polymeric networks found in molten silicates. SiO4 tetrahedrons are linked by bridging oxygens to form a wide range of structures. The presence of cationic network modifiers breaks down the network, forming non-bridging oxygens to maintain overall charge balance. The decrease in degree of polymerization leads to a decrease in viscosity. (alkali metal oxides, alkaline earth metal oxides or transition metal oxides.)
Calculation of change of exponent with increasing V content to modify Urbain equation

Graphs showing the relationship between viscosity (Pa.s) and temperature (°C) for different V contents:

- V0: $y = 3E+10e^{-0.014x}$, $R^2 = 0.9577$
- V15: $y = 3E+37e^{-0.058x}$, $R^2 = 0.9636$
- V25: $y = 2E+42e^{-0.066x}$, $R^2 = 0.9042$
- V35: $y = 2E+25e^{-0.034x}$, $R^2 = 0.9325$
Modification of exponent in Urbain equation

\[ y = 9E^{-0.05}x^2 - 0.0042x - 0.014 \]

\[ R^2 = 1 \]

Similar correlations can be developed using the cases with only Ni and Ni-V interaction.
But still need more data for good fits.
Some Preliminary Conclusions

- Ni and V content in slag increase slag viscosity
- V increased viscosity to a greater extent than Ni
- Reduction of V phases with oxidation of Fe phases and increase in crystal size contribute to viscosity increase
- Number of crystals increase with increasing NiO content thereby increasing slag viscosity
- Interaction occurs between V and Ni phases and leads to a further increase in viscosity
- Up to 20 % conversion of V2O5 to V₂O3 increases viscosity with increasing number of crystals
**Future work for reliable operation of gasifiers**

- Attempts to modify the Urbain equation to predict petcoke slag viscosity have been initiated. They will be refined as more data is collected.
- Interactions of V and Ni with Fe, Si, and other basic oxides need to be examined to understand the effect of blending with coal or other niche fuels.
- The phase diagrams for these must be incorporated into FactSage thermodynamic database for more accurate predictions slag phases for Petcoke and blends of Petcoke and coal.
Thank you very much!

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