The influence of added potassium compounds on the swelling behaviour of a high swelling South African coal under pyrolyzing conditions

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Introduction
South Africa: Need to use lower grade and swelling coals. Swelling of coal during the heating processes is due to physical and chemical changes [1-3]. Swelling is detrimental to most industrial reactors and a need to decrease swelling exists. Alkali and alkali earth metal salts (specifically the oxides, hydroxides and carbonates): catalytically active during coal thermal processing [4].

2KOH(s) → K₂O(s) + H₂O(g)
K₂CO₃(s) → K₂O(s) + CO₂(g)
Decomposition onset temperature = 900°C, melting point 905°C, evaporate [6, 7]
2K₂CO₃(s) → K₂O(s) + CO₂(CH₂)₃(g)
Decomposition onset temperature ~ 400-460°C [8]
KCl(s) → KCl(l)
Melting point = 773°C and evaporate easily

To investigate the influence of added alkali compounds on the swelling behaviour of a high swelling vitrinite-rich South African coal, potassium hydroxide (KOH), potassium chloride (KCl), potassium carbonate (K₂CO₃) and potassium acetate (K₂CH₃COO) were added to a partially demineralised sample.

Experimental
Vitrinite-rich coal: Tshikondeni mine, Limpopo Province, South Africa. < 75 µm and vacuum sealed.
Demineralized using a HCl/HF/HCl acid leaching technique [9]. Demineralized coal dried under vacuum at 60°C and stored in a desiccator under N₂.
XRF analyses - ASTM D4326 standard method.
Free swelling indices - ISO S01: 2003 standard method. 5 wt% potassium in coal-alkaline blends used.
TMA - SII Technology TMA/ SS6100 with EXSTAR6000. 10 wt% potassium in coal-alkaline blends used.
Dilatation - ASTM D5515 standard method

Results

Figure 1: Free swelling index numbers for the raw coal, demineralized coal and 5 Kwt% blends.

Table 1: Proximate analysis for the 8 coal samples with 10 Kwt% addition of potassium compounds for blends (air dried basis).

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Ash</th>
<th>% Fixed Carbon</th>
<th>% Inherent Moisture</th>
<th>% Volatiles</th>
<th>Matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw Coal</td>
<td>17.7</td>
<td>61.3</td>
<td>0.7</td>
<td>20.4</td>
<td>5.3</td>
</tr>
<tr>
<td>Demin Coal</td>
<td>17.7</td>
<td>61.3</td>
<td>0.7</td>
<td>20.4</td>
<td>5.3</td>
</tr>
<tr>
<td>KOH + Demin Coal</td>
<td>17.7</td>
<td>61.3</td>
<td>0.7</td>
<td>20.4</td>
<td>5.3</td>
</tr>
<tr>
<td>KCl + Demin Coal</td>
<td>17.7</td>
<td>61.3</td>
<td>0.7</td>
<td>20.4</td>
<td>5.3</td>
</tr>
<tr>
<td>K₂CO₃ + Demin Coal</td>
<td>17.7</td>
<td>61.3</td>
<td>0.7</td>
<td>20.4</td>
<td>5.3</td>
</tr>
<tr>
<td>K₂CH₃COO + Demin Coal</td>
<td>17.7</td>
<td>61.3</td>
<td>0.7</td>
<td>20.4</td>
<td>5.3</td>
</tr>
<tr>
<td>KOH + KCl + Demin Coal</td>
<td>17.7</td>
<td>61.3</td>
<td>0.7</td>
<td>20.4</td>
<td>5.3</td>
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Conclusions
Thermogravimetric analyses of the added compounds indicated that all of the potassium salts evaporate to some extent at different temperatures. It was found that the addition of KCl does not decrease the swelling or plastic properties of the coal. However, with the addition of the oxygen - containing potassium compounds to the demineralized coal, a decrease in the swelling was observed; with the addition of KCH₃COO showing the largest influence, followed by KOH and K₂CO₃. Dilatation results indicated that not all of the plastic properties of the coal were eliminated in the case of addition of KCH₃COO (as was for KCl), although KCH₃COO is also the decomposition product of KCH₃COO, K₂CO₃ starts to form from KCH₃COO at temperatures higher than the softening temperature of the coal. The main influence on the plastic properties of the added compounds thus seems to be crucial in the temperature range from 380°C to 480°C. The large decrease in the FSI value for the KClO₃ loaded demineralized coal sample seems to be due to a physical effect of forming a large amount of acetone vapour at the softening point of the coal, which ruptures the fluid coal pores, leading to a decrease in the FSI value. KCH₃COO decreases the plastic behaviour of the vitrinite-rich medium rank B coal to a larger extent than KCH₃COO.

References