THE HYDROPHOBIC CHARACTER OF PRETREATED COAL SURFACES

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INTRODUCTION

In recent years, the production of superclean coal has been of considerable interest in order to partially replace oil and natural gas as fuel sources. Of all the coal-cleaning processes, flotation is one of the most versatile. Carbon dioxide coal flotation is a new technology developed at the University of Utah. Compared with conventional flotation, carbon dioxide flotation enhances the ash rejection and increases flotation recovery for coals of different rank with the exception of lignite. However, significant improvement of the hydrophobicity and flotability of lignite has been found after controlled thermal pretreatment. The potential for the production of superclean coal by carbon dioxide has been demonstrated in bench scale flotation experiments.

EXPERIMENTAL

Coal samples and experimental methods of flotation, contact angle measurement and bubble attachment time measurement have been described in a previous paper. More recently, an attenuated total reflectance (ATR) accessory, the CIRCLE™ cell with a ZnSe rod from Spectra-Tech Inc., was used in ATR-FTIR spectroscopy. The coal for the ATR-FTIR analysis was ground to minus 1 micron in a ceramic mortar with distilled water at pH 6-6.5 before transferring to the CIRCLE™ cell at a coal/water ratio of 0.5 by weight. A spectrum for each coal was obtained by subtraction of water spectrum from the spectrum of the coal/water suspension. Both spectra were collected under the same conditions with the empty CIRCLE™ cell as a background.

RESULTS AND DISCUSSION

Coal Hydrophobicity

As shown in Figs. 1 and 2, it has been found by reagent-less Hallimond tube flotation and by contact angle and bubble attachment time measurements that the hydrophobicity and flotability of coals increase with an increase in coal rank, reaching a maximum for low-volatile bituminous coal and then decreasing with a further increase in coal rank. These traditional methods are excellent indicators of the macroscopic hydrophobicity of the coal surface. However, to better describe the hydrophobic/hydrophilic balance at a coal surface, it is important to establish the corresponding chemical characteristics of these coals.

DRIFT- and ATR-FTIR spectroscopy can provide a more detailed description of the coal surface than elemental bulk composition or chemically determined acid-group content as used by previous investigators. These two FTIR techniques have been used to evaluate the hydrophobicity of fine coals by a spectroscopic criterion—the hydrophilicity index—which contrasts the relative abundance of surface hydrophilic groups OH and COOM with the relative abundance of surface hydrophobic groups ArH and RH. Using the hydrophilicity index determined by both DRIFT- and ATR-FTIR spectroscopy, a rank-dependence of coal hydrophobicity can be plotted as shown in Fig. 2. Note that the hydrophobic character of coal estimated by the hydrophilicity index varies with coal rank in much the same fashion as bubble attachment time, contact angle, and flotation recovery. Since the coal rank is essentially classified by the carbon content, the hydrophilicity index determined by FTIR...
spectroscopy is obviously a more detailed index for evaluating coal hydrophobicity than coal rank or carbon content.

To ensure the surface sensitivity of the FTIR techniques and confirm the conclusions reached from the FTIR analysis, XPS has also been used to evaluate the hydrophobic character of fine coals. The ratio C/O determined by XPS has also been used to define a hydrophobicity index for the coals. Such a hydrophobicity index for six coals of different rank is presented in Fig. 1. Notice that the rank-dependence of coal hydrophobicity estimated by XPS agrees with that evaluated by other methods such as FTIR spectroscopy, flotation response, contact angle and bubble attachment time measurements.

Enhanced Hydrophobicity of Pretreated Coal

Characterization of C02-treated coal

As shown in Table 1, it has been found that C02 pretreatment increases coal hydrophobicity. Table 2 indicates that enhanced hydrophobicity of C02-pretreated coals results in an increased flotation recovery and enhanced ash rejection for coals of different rank with the exception of lignite. It has also been found that coals of middle ranks such as high-, medium-, and low-volatile bituminous coals are most amenable to carbon dioxide coal flotation.(5)

Oxidation can result in a reduced hydrophobicity of C02-pretreated coals. Figure 3 illustrates that oxidation of a C02-pretreated low-volatile bituminous coal in air reduces the coal hydrophobicity and restores the original lower hydrophobic character after about 20 hours of oxidation. Fortunately, coal oxidation is a slow process. No significant loss in coal hydrophobicity was observed during the first couple hours which was long enough to complete flotation experiments.

The success of C02 coal flotation has been attributed to the coal's high adsorption potential for C02.(6) It has been found by monitoring the OH absorption band using in-situ FTIR spectroscopy that pore water and hydration water in coal are displaced by C02 during pressure treatment, which results in enhanced coal hydrophobicity as shown in Fig. 4.

A model for carbon dioxide adsorption by coal is being considered, and a schematic drawing of the microstructure is shown in Fig. 5. This drawing represents a final state of the adsorption process, where all the pore water and hydration water have been replaced by C02. Before C02 pretreatment, the positions of C02 molecules in this drawing are predominantly occupied by H2O molecules. Displacement of the H2O molecules by C02 molecules during pressure treatment and C02 nanobubble formation at the coal surface on pressure release are believed to be responsible for the improved flotation performance.

Characterization of thermally-treated coal

It has been found that low-temperature thermal treatment significantly increases the hydrophobicity of lignite as suggested by FTIR hydrophilicity index determinations and confirmed by bubble attachment time measurements/flotation response (see Fig. 6). It is believed that the increased hydrophobicity of lignite is attributed to the removal of pore water, hydration water and some organic OH functional groups as well as the diffusion of volatile matter to the surface and the reorientation of surface functional groups. As shown in Table 2, it has been found that controlled thermal treatment can also increase the hydrophobicity of subbituminous coal and anthracite. Finally it should be noted that the thermal treatment improves the flotation separation of lignite from mineral matter.

SUMMARY

Increased hydrophobicity and hence the flotability of coals of different rank has been observed for CO2 pretreatment and/or controlled thermal pretreatment. DRIFT- and ATR-FTIR and XPS techniques have been used to determine the surface chemical characteristics in order to evaluate coal hydrophobicity. These results agree very well with those determined by traditional methods. The enhanced hydrophobicity of C02-treated coal is attributed to the high specific affinity of coal for C02 which results in the displacement of pore water and hydration water by C02 and on pressure release leads to nanobubble formation at the coal surface in aqueous suspension. Increased hydrophobicity of
lignite by thermal treatment arises from the removal of pore water, hydration water and some organic OH functional groups as well as the diffusion of volatile matter to the surface and the reorientation of surface functional groups.

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REFERENCES

Table 1  Contact Angle and Bubble Attachment Time for Different Gas Bubbles on a Polished Surface of Low-Volatile Bituminous Coal

<table>
<thead>
<tr>
<th>Pressure Treatment Using Corresponding Gas Phase at 20 psi</th>
<th>Gas Phase of Bubbles</th>
<th>Contact Angle (degrees)</th>
<th>Bubble Attachment Time (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yes</td>
<td>Air</td>
<td>49-52</td>
<td>170-190</td>
</tr>
<tr>
<td>Yes</td>
<td>N₂</td>
<td>50-51</td>
<td>140-160</td>
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<tr>
<td>Yes</td>
<td>CO₂</td>
<td>54-56</td>
<td>20-25</td>
</tr>
<tr>
<td>No</td>
<td>Air</td>
<td>47-49</td>
<td>180-200</td>
</tr>
<tr>
<td>No</td>
<td>N₂</td>
<td>50-51</td>
<td>170-190</td>
</tr>
<tr>
<td>No</td>
<td>CO₂</td>
<td>51-53</td>
<td>140-150</td>
</tr>
</tbody>
</table>

Table 2  Enhanced Hydrophobicity and Improved Flotation Performance of Pretreated Coals of Different Rank

<table>
<thead>
<tr>
<th>Coal Rank</th>
<th>Ratio of Attachment Times $\frac{T_{CO₂}}{T_{air}}$</th>
<th>Increased Flotation Recovery by CO₂ Pretreatment</th>
<th>Enhanced Ash Rejection by CO₂ Pretreatment</th>
<th>Increased Hydrophobicity by thermal Pretreatment</th>
<th>Enhanced Ash Rejection by thermal Pretreatment</th>
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<tbody>
<tr>
<td>ANT</td>
<td>0.70</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
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<tr>
<td>LVB</td>
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<td>Yes</td>
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<tr>
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<tr>
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<tr>
<td>SUB</td>
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<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td></td>
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<tr>
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</table>
Figure 1 Coal hydrophobicity evaluated by Hallimond tube flotation, contact angle measurement, and XPS analysis as a function of coal rank. ANT = Anthracite, LVB = Low-volatile bituminous coal, MVB = Medium-volatile bituminous coal, HVB = High-volatile bituminous coal, SUB = Subbituminous coal, LIG = Lignite.

Figure 2 Hydrophobic character of coal as described by bubble attachment time and the hydrophilicity index determined from DRIFT- and ATR-FTIR spectra.
Pressurized by Air (20 psi), aged in Air, air Bubble

Pressurized by CO₂ (20 psi), aged in air, CO₂ bubble

Pressurized by CO₂ (20 psi), aged in N₂, CO₂ bubble

Figure 3 Bubble attachment time measured on the polished surface of a pretreated low-volatile bituminous coal as a function of aging time of the coal.

Figure 4 The hydrophilicity index of a CO₂-pretreated high-volatile bituminous coal (-5 micron) at 302 °K determined by DRIFT-FTIR spectroscopy as a function of CO₂-coal interaction time.
Figure 5  Schematic drawing of carbon dioxide adsorption by coal.

Figure 6  Hydrophobic character of lignite evaluated by the DRIFT-FTIR hydrophilicity index, bubble attachment time and flotation recovery as a function of thermal-treatment time. (3)