A NEW MODEL OF COAL-WATER INTERACTION AND RELEVANCE FOR DEWATERING

E. M. SUUBERG (PRINCIPAL INVESTIGATOR)
Y. YUN, W.D. LILLY (STAFF)
K. LEUNG AND TOM GATES (STUDENTS)

DIVISION OF ENGINEERING
BROWN UNIVERSITY
PROVIDENCE, RI 02912
TEL. (401) 863-1420

QUARTERLY TECHNICAL PROGRESS REPORT
1 DECEMBER- FEBRUARY, 1993

PREPARED FOR:
U. S. DEPT. OF ENERGY
PITTSBURGH ENERGY TECHNOLOGY CENTER
P.O. BOX 10940
PITTSBURGH, PA 15236

DR. WU-WEY WEN
TECHNICAL PROJECT OFFICER

"US/DOE Patent Clearance is not required prior to the publication of this document"
Project Overview

This project is concerned with a basic scientific question concerning the properties of coal— to what extent is the ability of coal to hold moisture a manifestation of the well-known ability of coal to swell, when exposed to good solvents? The question implies that the long-held belief that coal holds a significant portion of its moisture by classical capillary condensation processes, is possibly in error. This seems to be a very real possibility for low rank coals- i.e. lignites. To explore this hypothesis further requires an examination of the basic phenomena governing the swelling of coals in good solvents. This is the focus of the first part of this project.

The possibility that coal holds a significant portion of its moisture by solvent swelling mechanisms leads to an interesting technical issue. It is well known that simple drying of low rank coals at minemouth is ineffective because the process is reversible, to a significant degree. The economic advantages of pre-shipment drying have however dictated a search for "permanent" drying procedures. These have been developed by largely empirical means, and involve mild pyrolytic treatments of the coals in oil, steam or liquid water itself. The idea has always been to pyrolytically remove oxygen groups, which are assumed to be those that hold water most strongly by hydrogen bonding. The treatments have been designed to minimize tar formation and decrepitation of the particles, both highly undesirable. In relation to the present new hypothesis concerning water retention, it is likely that a sound approach to permanent drying would involve highly crosslinking the coal at mild drying conditions. The crosslinked coal could not swell sufficiently to hold much water. It is identifying processes to achieve this goal, that constitute the objective of the second phase of this work.

Current Quarter Summary

This quarter's efforts involved continuing to use the flow microcalorimeter as a tool for characterizing the heat effects involved in interaction of swelling solvents and coals. These data are of relevance to the overall project goal of establishing that moisture retention is a solvent swelling
process. To this end, it is necessary to get reliable data on the heat effects of coal-solvent interaction, so that partial molar enthalpy of mixing curves can be constructed. The choice to work initially with solvents in addition to water merely is consistent with the viewpoint that the phenomena are indeed generic with respect to solvent, even though the solvents chosen all interact with specific sites in the coals.

During the last quarter, we achieved success at establishing the flow microcalorimetric device as a reliable tool for determining the heat effects of solvent-coal interactions. Earlier concerns about spurious heat effects due to instrument design were proven groundless. The results that were obtained did point out the enormous sensitivity of the results to the method of preparation of the sample. Both oxidation and sample drying were clearly established as important effects. The subtle ways in which these effects could cloud interpretation of the results were explored.

During this quarter, we used the flow microcalorimeter to explore heat effects as a function of concentration of solute. Earlier results had strongly suggested that the heat effect is large in going from zero to small concentrations, but that once the concentration was above a low levels, there would be relatively small effects of concentration.

Next Quarter Plans

We hope to revisit the model of coal swelling, armed with the new, more reliable data on the heat effects of coal-solvent interactions. The surprisingly high values of heat effect when coal was contacted with small amounts of fresh, specifically interacting solvents, need to be better understood.

1.0 INTRODUCTION

The flow microcalorimeter provides measurements of the heat effects seen when mixing coal and solvents. Our approach here was to again, use small amounts of a specifically interacting solvent in a weakly interacting solvent (here, n-heptane). The experiment consisted of creating a step change in concentration from pure heptane to the mixture, and following the heat effect of
adsorption, and then reversing the step change and following the reverse process of desorption.

2.0 EXPERIMENTAL

The flow microcalorimeter is a commercial device (Microscal, Ltd.), used here in an unmodified form. Briefly, it consists of a tube maintained in a carefully controlled thermal environment, which is instrumented with calibrated thermistors, capable of showing very small heat effects within the tube. The tube is packed with a few tens of milligrams of coal, and a flow of solvent is introduced, at carefully controlled rate through the bed. Again, the experiments involved establishing a steady flow of non-specifically interacting solvent (e.g. heptane) through the coal sample bed, and then switching this flow to another strongly interacting solvent, and measuring the resultant heat release. Cycling back and forth between heptane and the strongly interacting solvent gives a measure of the reversibility of the sorption process involving the strongly interacting solvent. For a fully reversible sorption process, the integrated heat release during adsorption should exactly balance the heat absorption during desorption.

The preparation of the coal has a significant effect on the results obtained. Here, all results will be reported on the Argonne National Laboratory Premium Coal Sample Beulah Zap lignite. The particular aspects of sample preparation will be discussed in connection with the results outlined below.

It should be noted that one of the main concerns in performing such tests is that coals will swell when exposed to specifically interacting solvents. This is, of course, precisely the effect that we are interested in studying. Significant swelling will be a major problem, since the sample cell in the flow microcalorimeter is of finite volume, and attached to very small tubes that carry the pure liquids into and out of the cell. Significant swelling will cause loss of void volume causing the pressure drop through the cell to increase to the point that a constant flowrate cannot be maintained by the syringe pumps feeding the liquids, and it can damage the filters at the exits of the cell. Therefore it was always necessary to pack the cell such that there would be at least 10% void volume within the cell, to allow for expansion during uptake of the specifically interacting solvent. It should also be kept in mind that the normal volumetric swelling ratio of this coal in water is
approximately 1.3 (i.e. 30% increase in volume) and in alcohols a comparable value is obtained. In even stronger solvents such as pyridine, a swelling ratio of over 2 (i.e. >100% swelling) is seen.

Thus the experiments that we are performing here cannot be safely carried out by switching between a weak solvent and a pure specifically interacting solvent. The use of “inert” fillers mixed with the coal, so as to keep the percentage swelling low, is also problematic; no material that we have thus far tested gives a low enough heat of adsorption, so as to not raise questions about the accuracy of the results for the coal. Therefore we work with “neat” coal samples, and keep the swelling low by keeping concentration jumps small. It is possible to measure heat effects at high concentrations of specifically interacting solvent, by first preswelling the sample outside of the cell in a slightly lower concentration mixture.

3.0 RESULTS

First, it is necessary to correct three data points reported in the previous quarterly. Table 1 shows the corrected data for experiments performed with 1% propanol in heptane solution. The correction involves the characterization of the samples with respect to drying. Experiments 12-20 involved use of samples dried in-situ in the flow microcalorimeter, at about 323 K, under vacuum. It had been previously reported that these samples had not been dried at all.

In this quarter, attention turned to how the heat effects observed during swelling depend upon concentration of the specifically interacting solvent. This work was again performed initially with 1-propanol/ n-heptane mixtures, in which the propanol is the specifically interacting solvent. The first question which had to be answered was how large a propanol concentration jump could be tolerated in the microcalorimeter, bearing in mind the problems associated with excessive swelling in the calorimeter flow cell. For this purpose, a series of ordinary solvent swelling experiments were performed, in which the coal was immersed in various solvent mixtures, and the volumetric swelling of the sample was determined from the height of the (centrifuged) column of coal in a constant diameter glass tube. The results are seen in Figure 1.

Figure 1 shows a monotonic increase in volumetric swelling ratio with concentration of propanol in the mixture. It is noted that even heptane itself is able to swell the coal a bit (4%)
relative to the initial dry state, since the coal had been previously pyridine extracted. The propanol swells the coal by somewhat over 30% when pure, which is typical also of the extent of swelling of this coal by water.

Figure 2 shows the same data as in Figure 1, but plotted in terms of the logarithm of propanol concentration. A crudely linear fit is seen. This is strongly suggestive of the fact that the solvent swelling is varying with the chemical potential of the propanol in solution, since for ideal solutions, the chemical potential varies with concentration according to:

$$\mu_i = \mu_i^0 (T,P) + RT \ln x_i$$

where $\mu_i$ is the chemical potential of component $i$ and $x_i$ is its mole fraction in the solution, and $\mu_i^0$ is pure $i$ Gibbs free energy at the same temperature and pressure as the solution. Since the crude approximation of ideal solution behavior may be valid, it is useful to recall that in an ideal solution, the partial molar enthalpy of any component is equal to pure component molar enthalpy. Thus each increment of propanol added to the structure would result in a molar heat effect relative to the same base value, and one would be able to determine the enthalpy needed to relax the coal structure to a configuration able to accept the increment of solvent.

Measuring the heat effects in an experiment in which the propanol concentration was changed from 5% to 10% by volume proved very challenging, because of the small magnitude of the heat effect. The overall heat effect was 0.34 J/g of lignite, obtained as usual by averaging experiments involving adsorption and desorption. The heat effects were, on an absolute scale, the order of 3 $\mu$W in these experiments, and the instrument resolution is only $1\mu$W. Therefore the attempts to study the heat effects by this method are fraught with large uncertainties.

Nevertheless, the values obtained from the above experiments allowed us to draw some useful conclusions. First, the magnitudes of heat effects seen as the sample reaches pure solvent swelling equilibrium are quite small. This means, as we have earlier suggested, that the partial molar enthalpy near pure solvent swelling equilibrium is very nearly zero. The swelling process, at that point, is effectively entropically driven to completion.

Attempts were made to measure the actual uptake of propanol using a liquid chromatographic detector, measuring the deficit of propanol in the liquid leaving the flow cell.
Unfortunately, a failure in the electronics of the detector prevented us from successfully performing the measurements, and required us to estimate the mass uptake from swelling data.

The amount of extra solvent uptake per mass of coal, in swelling from the 5% to the 10% propanol equilibrium condition, can be estimated from: \[ \Delta m/m_c = \Delta Q (\rho_s/\rho_c) \], where \( \rho_s \) represents the solvent density and \( \rho_c \) represents the coal density. From the measured swelling values, and assuming that the pure solvent density can be used for this calculation, then about 3% by mass solvent is taken up in the additional swelling. This means that the enthalpy of mixing is about 11 J/g of propanol uptake, or about 680 J/mole of propanol. The calculation is admittedly crude, but shows that the heat effect is much smaller than ordinary hydrogen bonding interactions. This is no particular surprise, since the propanol and coal might merely be trading hydrogen bonding partners, rather than creating new bonding opportunities. That is, the coal is initially internally hydrogen bonded, and there is probably some hydrogen bonding between propanol molecules in solution as well. When the propanol hydrogen bonds with the coal, the other hydrogen bonding interactions must be broken, at the cost of some energy, which offsets some of the gain from the new bonding opportunities.

The above results quickly convinced us of the futility of proceeding with concentration jump experiments with propanol in heptane. The heat effects were simply too small to measure at higher propanol concentrations. Attention was then turned to a more strongly interacting solvent, to see if it would exhibit the same behavior. The pyridine/n-heptane system was thus chosen for examination.

The swelling behavior of the Beulah lignite is shown in Figures 3 and 4, which are analogous to those presented earlier for propanol swelling. While the data are more scattered, the same general behavior is observed. Note, however, that the pyridine is a stronger swelling solvent, as the swelling ratios are somewhat higher than those obtained with propanol mixtures of comparable concentration.

Table 2 presents the results of the calorimetric measurements on the pyridine/heptane system. The results are upon first examination rather peculiar, in that the trend with concentration is not very consistent. A rather modest value of the enthalpy of mixing is implied in going from 10% pyridine to 15% pyridine solutions, but a steep jump is seen in going from 15% to 20%.
Again a more modest jump is seen between 20% and 25%, and a steep increase between 25% and 35%. This suggests rather complicated mixing behavior is involved. It may well be that the jumps reveal particular types of interaction processes coming into play; that is, the pyridine may be titrating certain sites as its chemical potential increases. Alternatively, the solution of pyridine in heptane is not likely to be nearly ideal, and the abrupt changes that are seen could also have an origin in what happens to the chemical potential of the pyridine in solution, in certain concentration ranges. This requires more study.

It is again possible to estimate, from swelling data, in the manner described above, the uptake of pyridine associated with some of the heat effects. For example, in going from 10% to 20% pyridine solution, the uptake is estimated to be about 5% by mass, so the average heat effect per mol of pyridine sorbed is 9.5 kJ. This is quite a bit larger than the heat effect with the propanol, showing that the pyridine is indeed capable of energetically more favorable interactions. As of this time, no other tests have been performed with the pyridine systems, so it is not possible to say yet whether the same conclusion concerning the small magnitude of partial molar enthalpy of mixing applies in this case as well.

4.0 CONCLUSIONS

It is clear that most heat is released during the uptake of solvent from propanol/heptane mixtures of low propanol content, and therefore, of low propanol chemical potential. Increasing the chemical potential of the propanol results in little more uptake and little heat release. This seemingly means that near solvent swelling equilibrium in pure solvent, the partial molar enthalpy of mixing is small.

Some very large heat effects reported for immersion of the Beulch lignite (105 J/g coal, in pure pyridine1) are much larger than those observed here for step changes in concentration. Thus the conclusion is again, that the partial molar enthalpy of mixing of pyridine with this coal may not be that large, near pure solvent swelling equilibrium.

1 Gunkowski, M; Liu, Q.; Arnett, E., Energy and Fuels, 1988, 2, 295.
Table 1
Summary of Heats of Adsorption and Desorption on Beulah Lignite of 1-propanol from 1% Solution in n-heptane

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp.(K)</th>
<th>$\Delta H_a$(J/g)$^1$</th>
<th>$\Delta H_d$(J/g)$^1$</th>
<th>$\Delta H_a$(J/g)$^2$</th>
<th>$\Delta H_d$(J/g)$^2$</th>
<th>$\Delta H_a$(J/g)$^m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undried, unextracted (-400/9)$^a$</td>
<td>325</td>
<td>-26.3</td>
<td>26.3</td>
<td>-25.0</td>
<td>27.9</td>
<td>-26.4</td>
</tr>
<tr>
<td>Dried$^e$, unextracted (-400/12)</td>
<td>329</td>
<td>-24.2</td>
<td>26.2</td>
<td>-29.0</td>
<td>28.4</td>
<td>-27.0</td>
</tr>
<tr>
<td>Dried$^b$, unextracted (-200/27)</td>
<td>329</td>
<td>-44.0</td>
<td>39.3</td>
<td>-44.6</td>
<td>38.1</td>
<td>-41.5</td>
</tr>
<tr>
<td>Dried$^b$, extracted (-400/r7)</td>
<td>330</td>
<td>-52.8</td>
<td>40.1</td>
<td>-51.2</td>
<td>40.0</td>
<td>-46.0</td>
</tr>
<tr>
<td>Dried$^c$, extracted (-400/v1)</td>
<td>333</td>
<td>-35.1</td>
<td>32.5</td>
<td>-35.3</td>
<td>33.5</td>
<td>-34.8</td>
</tr>
<tr>
<td>Undried, unextracted (-400/6)</td>
<td>311</td>
<td>-29.4</td>
<td>23.2</td>
<td>-20.7</td>
<td>29.9</td>
<td>-25.8</td>
</tr>
<tr>
<td>Dried$^e$, unextracted (-400/15)</td>
<td>313</td>
<td>-29.5</td>
<td>35.2</td>
<td>-33.2</td>
<td>29.4</td>
<td>-31.8</td>
</tr>
<tr>
<td>Dried$^b$, unextracted (-200/25)</td>
<td>312</td>
<td>-24.3</td>
<td>27.9</td>
<td>-30.3</td>
<td>30.8</td>
<td>-28.3</td>
</tr>
<tr>
<td>Dried$^b$, extracted (-400/r4)</td>
<td>318</td>
<td>-44.4</td>
<td>47.4</td>
<td>-54.9</td>
<td>45.5</td>
<td>-48.1</td>
</tr>
<tr>
<td>Undried, unextracted (-400/4)</td>
<td>300</td>
<td>-13.7</td>
<td>11.8</td>
<td>-13.0</td>
<td>10.5</td>
<td>-12.3</td>
</tr>
<tr>
<td>Dried$^e$, unextracted (-400/18)</td>
<td>298</td>
<td>-17.8</td>
<td>15.4</td>
<td>-18.1</td>
<td>17.6</td>
<td>-17.2</td>
</tr>
<tr>
<td>Dried$^d$, unextracted (-400/21)</td>
<td>299</td>
<td>-16.7</td>
<td>17.0</td>
<td>-11.1</td>
<td>15.8</td>
<td>-15.2</td>
</tr>
<tr>
<td>Dried$^b$, unextracted (-200/23)</td>
<td>297</td>
<td>-10.3</td>
<td>12.4</td>
<td>-14.2</td>
<td>15.9</td>
<td>-13.2</td>
</tr>
<tr>
<td>Dried$^b$, unextracted (-200/29)</td>
<td>297</td>
<td>-22.8</td>
<td>24.3</td>
<td>-22.4</td>
<td>21.4</td>
<td>-22.7</td>
</tr>
<tr>
<td>Dried$^b$, extracted (-400/r1)</td>
<td>297</td>
<td>-13.9</td>
<td>26.8</td>
<td>-19.4</td>
<td>25.0</td>
<td>-21.2</td>
</tr>
</tbody>
</table>

1. Refers to first cycle of adsorption ($\Delta H_a$) and desorption ($\Delta H_d$). 2. refers to second cycle.

m. Refers to average heats of adsorption of the alcohol from the alkane carrier.

a. First values in parentheses refer to mesh size of particles, second to experiment numbers.
b. Vacuum oven-dried at 345 K.
c. Vacuum dried, in-situ in the flow microcalorimeter, at 343 K.
d. Vacuum oven-dried, at room temperature.
e. Vacuum dried, in-situ in the flow microcalorimeter, at 323 K.
### Table 2

**Summary of Heats of Adsorption and Desorption on Beulah Lignite of Pyridine from Solutions of Pyridine in n-heptane**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temp.(K)</th>
<th>$\Delta H_a (\text{J/g})^1$</th>
<th>$\Delta H_d (\text{J/g})^1$</th>
<th>$\Delta H_a (\text{J/g})^2$</th>
<th>$\Delta H_d (\text{J/g})^2$</th>
<th>$\Delta H_a (\text{J/g})^m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% to 12% pyridine</td>
<td>304</td>
<td>-0.67</td>
<td>0.38</td>
<td>-0.63</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>Dried, extracted (-400/pr10)$^a$</td>
<td></td>
<td>-0.64</td>
<td>0.44</td>
<td>-0.68</td>
<td>0.41</td>
<td>-0.52</td>
</tr>
<tr>
<td>12% to 15% pyridine</td>
<td>303</td>
<td>-1.04</td>
<td>0.59</td>
<td>-0.83</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>as above (-400/pr12)</td>
<td></td>
<td>-0.99</td>
<td>0.64</td>
<td>-0.81</td>
<td>0.67</td>
<td>-0.78</td>
</tr>
<tr>
<td>15% to 20% pyridine</td>
<td>303</td>
<td>-6.14</td>
<td>6.65</td>
<td>-5.65</td>
<td>5.06</td>
<td>-5.88</td>
</tr>
<tr>
<td>as above (-400/pr15)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20% to 25% pyridine</td>
<td>302</td>
<td>-2.16</td>
<td>0.80</td>
<td>-2.12</td>
<td>0.83</td>
<td></td>
</tr>
<tr>
<td>as above (-400/pr20)</td>
<td></td>
<td>-1.95</td>
<td>0.76</td>
<td>-1.76</td>
<td>--</td>
<td>-1.48</td>
</tr>
<tr>
<td>25% to 35% pyridine</td>
<td>304</td>
<td>-6.18</td>
<td>6.02</td>
<td>-5.00</td>
<td>--</td>
<td>-5.70</td>
</tr>
<tr>
<td>as above (-400/pr25)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a. Notes as in Table 1.*
Figure 1. Volumetric swelling ratio of extracted, dried Beulah lignite in 1-propanol/n-heptane mixtures (swelling after 24 hours).
Figure 3. Volumetric swelling ratio of dried, pyridine extracted Beulah lignite in pyridine/n-heptane mixtures. Swelling ratios measured after 48 hr.
Figure 2. Volumetric swelling ratio of Beulah lignite in 1-propanol/ n-heptane mixtures. Graph illustrates that the swelling is roughly proportional to logarithm of propanol concentration.
Figure 4. Volumetric Swelling Ratio of Beulah lignite as a function of the logarithm of pyridine concentration. These are the same data as in Figure 3.