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

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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 carrying forward the examination of the studies that seek to

establish whether moisture retention is indeed a solvent swelling phenomenon. The new data presented here are related to the ability of coals to exhibit colloidal shrinking/swelling behavior. These data are considered in the context of earlier obtained data on the isotherms for moisture retention, and the heat effects associated with moisture retention, discussed in the previous quarterly report.

Next Quarter Plans

The plans for the next quarter call for investigating the very important questions concerning the partial molar free energies of wetting of the coal by water and other solvents. These measurements were begun, as scheduled, in this quarter, but have not yet yielded reliable results and thus have not yet been reported. It is only with these quantities better characterized that the further development of the governing theory will be possible.

1.0 INTRODUCTION

This report is, again, 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.

The fact that coal has a colloidal gel-like structure that can shrink and swell in response to moisture loss and gain is well established [1-4]. The fact that water can be held by polar groups within the structure of coal also is well documented [5]. There is considerable experimental evidence that there are at least two mechanisms by which water is held in coals. Differential scanning calorimetry (DSC) has suggested that water is held in a tightly bound "unfreezable" form as well as in a bulk "freezable" form [6,7]. Another study, based on proton NMR examination of the water associated with a brown coal, reached similar conclusions [8]. The water is present in a free phase and a bound phase, the latter water molecules having some "mobility" and an ability to exchange with one another on a timescale of a typical experiment (order of fractions of a millisecond). The apparent freezing temperature of the bulk water is a bit below 273K (consistent with other results [6,7,9]), and decreases with heat treatment of the coal [8].

There has also been indirect evidence from dehydration experiments to support the view that water exists in several forms in coal. Variations in the extent of shrinkage brown coal per unit of moisture removed have been interpreted in terms of the role of different types of moisture in coal [1]. The isosteric heat of moisture sorption on coals has been observed to be a function of amount of water in the coal [10]. The fact that hysteresis in coal moisture sorption isotherms must be determined by shrinkage and swelling effects [11] complicates interpretation of such data, however. Perhaps one of the simplest illustrations of the multifaceted nature of water in coals has been provided by the observation that the dehydration behavior as a function of time is not particularly simple [12- 14]. There is a suggestion from recent data that the process of moisture loss may be second order [13] or of apparent order between 1.3 and 2.4 relative to remaining water in the case of bound water [14].

It thus appears that water is retained tightly and in several forms in coals and that coal behaves like a swellable colloid in the presence of water. These two facts have not yet been merged into a unified theory of water retention in coals.

First, we address the question of how well does the shrinking/swelling colloid model apply to coals other than lignites? Do bituminous coals also collapse upon drying, or is this kind of behavior limited to lower ranks? We use the direct evidence from shrinkage upon drying, as well as indirect evidence provided by experiments on transport of solvents through coals to suggest that bituminous coals do indeed exhibit the colloidal behavior.

2.0 EXPERIMENTAL

The data to be considered in this paper were obtained by a variety of techniques. The data were all obtained on the coals shown in Table 1. There were many different sources for these samples, and the samples were available in many different conditions. Some had been carefully stored in large lump form, and were ground immediately prior to use. These had dried to only a limited extent prior to testing. Others had been stored in various ground forms, and had dried somewhat before use. The conclusions concerning shrinkage upon drying were not found to be particularly sensitive to the initial condition of the samples used for the tests. This will be established below. This does not, however, imply that the changes that occur upon drying are minor; quite the opposite is true, as we have already noted [4].

The first measurements to be reported here involved drying the coals in a vacuum oven, so as to prevent oxidation during drying. The samples were typically ground to less than 600 μ m particle diameter and measured into thin glass tubes, quickly centrifuged so as to settle the samples, and then they were placed into the vacuum oven at either room temperature (298K) or at 373K. The samples were then tracked with respect to mass loss and volumetric shrinkage. The precision of the volumetric shrinkage measurements is no better than 2% (absolute), the mass loss measurements are good to 0.1%.

Classical water sorption isotherms were measured on finely ground samples, by ordinary gravimetric techniques, as earlier described [4].

Differential scanning calorimetric (DSC) measurements were performed on Beulah lignite

samples, to explore the concept of a distribution of different energy sites for holding moisture in the coal. These experiments were performed in a TA Instruments 2910 DSC, by placing initially wet Beulah lignite samples into DSC pans that had holes in them to provide facile loss of water from the pans. Samples were heated up to a particular temperature, cooled, and reheated to a higher temperature, to explore the magnitude of mass loss and heat effects associated with moisture loss in various temperature intervals.

3.0 RESULTS

3.1 SHRINKAGE UPON DRYING

The volumetric shrinkage of the samples was excellently correlated with the moisture loss from the samples. This is readily seen from Figure 1, which was obtained by drying the coals of Table 1 at 373 K. The correlation for the data can be expressed as:

$$\text{Volumetric Shrinkage (\%)} = -0.162 + 0.863 (\text{Moisture Loss, \%})$$

A second series of measurements was performed on a Beulah lignite (the first sample in Table 1). The lignite was allowed to partially dry at room temperature over various aqueous solutions of differing dessicant strength (e.g. H_2SO_4 , KCl , see ref. 4). The partially dried samples were then subjected to the same type of tests described above, both at room temperature and at 373 K. These results are shown in Figure 2. The same type of linear trend is seen as in Figure 1. There is a bit of a tendency for the shrinkage to be larger on the initially wetter samples dried at 298 K, but the differences are small enough so that their significance is open to question, given the uncertainty in the measurements.

As before, the correlation shown in Figure 2 is seen to be well approximated by a linear relationship:

$$\text{Volumetric Shrinkage (\%)} = a + b (\text{Moisture Loss, \%})$$

In the case of the results of Figure 2, $a = 0.803$, $b = 0.900$. Other similar tests were performed at room temperature with Gascoyne lignite ($a = -0.182$, $b = 1.00$), with Freedom lignite ($a = 0.230$, $b = 1.07$) and with Glenn Harold lignite ($a = 0.386$, $b = 0.938$). These results suggest that earlier reported shrinkage data [4], which were obtained by measurements on larger blocks of coal, might have been influenced by the existence of residual mechanical stresses

within the large sample blocks. The earlier results had not as clearly defined a linear relationship between moisture removed and volumetric shrinkage, but were otherwise in reasonable agreement with the present results.

The volumetric shrinkage relationship shown above may be recast as:

$$(M_C + M_W)/(V_C + V_m) = a' M_C/(V_W - V_p) + (a' + b) M_W/(V_W - V_p)$$

where M_C is the mass of dry coal and M_W is the mass of water in the sample, the V 's refer to the volumes that these materials occupy, and V_p is the volume of porosity created upon drying. It should be noted that in this representation, the numerical value of b is as above, and $a' = a/100$. For all reasonable values of the parameters, the first term on the right hand side is generally small compared to the second, and will be neglected. Also $b \gg a'$. The left hand side is the bed-moist bulk density of the coals, and has been earlier measured to be of order 1.2 g/cc [4]. This leads to the conclusion that:

$$1/(1.2) = 0.833 \text{ cc/g} = 1/b - V_p/(bM_W)$$

where the density of the water in coal is taken to be roughly its bulk density (1 g/cc). Thus the porosity of the dried sample may be calculated from:

$$V_p/M_C = (M_W/M_C) (1 - 0.833 b) \text{ cc/g}$$

For a typical initial lignite moisture content of 30%, $M_W/M_C = 0.43$, and the porosity of the dried coal would be estimated as between 0.11 cc/g for the Beulah lignite and 0.05 cc/g for the Freedom lignite. The calculations are crude, but the results are in quite reasonable agreement with measurements of the porosity of dried lignites [22]. The ratio of volumetric porosity development to volumetric moisture loss is given by an expression $[1 - bf_m/f_v]$, where f_m is the mass fraction moisture in the coal, and f_v is the volume fraction of moisture in the coal. Again, linear volume additivity will almost surely not apply, but this equation suggests that for reasonable estimates of the parameters (f_m/f_v should be just a bit more than unity) and the measured values of b , the porosity development will not be nearly as great as the volumetric loss of moisture. Applied to a high volatile bituminous coal of 1.5% moisture content and initial density of 1.3 g/cc, the final porosity prediction would be unreasonably low (0.005 cc/g), so the conclusion is that the porosity had to already be present, rather than being created by moisture loss. This is obvious if one considers even from a simple volumetric pore filling perspective how much porosity could be created by loss of 1.5 % moisture in the form of 1 g/cc bulk water; there is not nearly enough volume lost so as to create porosity of order

0.1cc/g, as is typically reported [22].

What the above results imply is that the lower rank coals will behave quite like ordinary colloidal gels. They cannot completely collapse to a zero porosity solid upon drying. The higher rank coals also show distinctly colloidal shrinkage behavior, but have in coalification collapsed to a point at which open porosity has already been created. The fact that the structure of the coals in all cases significantly expands to accomodate moisture suggests that simple capillary condensation models of moisture retention are inadequate for describing the thermodynamics of the situation. There must be significant thermodynamic consequences associated with the elastic deformations of the coal's network structure that are not properly allowed for in a capillary condensation approach. Such issues have been reviewed in connection with solvent swelling measurements of coal structure [19,23].

3.2 SORPTION ISOTHERMS OF WATER ON THE NORTH DAKOTA LIGNITES

In the previous quarter, the results of tests performed to determine the sorption isotherms on the same samples were reported. It has been noted [e.g.15] that the moisture loss from coal increases with drying temperature, even above 373 K. This supports the idea that there is a distribution of energies associated with water retention and that some water is held more strongly in coal than in pure bulk water. Just how much more strongly is revealed by these types of experiments. Sorption isotherms were measured as earlier described [4] and results are given in Fig. 3.

The fact that the isotherms do not shift at all (Beulah) or very little with temperature means that the isosteric heat of moisture sorption is close to the heat of condensation of pure water (i.e. 42.7 kJ/mol). The "isosteric" heat is as usual determined from:

$$[\partial \ln (P/P_0) / \partial T]_n = (q_{st} - q_{cond})/RT^2$$

where P/P_0 is the vapor pressure of water relative to saturation (i.e. the relative humidity), T is temperature, the subscript n implies evaluation of the derivative at constant moisture loading, q_{st} is the isosteric heat (positive is exothermic), q_{cond} is the (positive) latent heat of condensation of water, and R is the gas constant. There is a danger in using here the term "isosteric" heat, in that it might imply the usual situation of a surface condensation process. As discussed above, we do not believe that this is the nature of the process, and interpret the

quantity as simply indicating a heat at constant moisture uptake.

When there is a shift of isotherms in the data of Fig. 3, between 303 K and 323 K, the results imply isosteric heats of order 70 kJ/mol or less. In fact, there is reason to believe that the apparent shift in the isotherms could be an artifact of thermally induced crosslinking even at these low temperatures; the solvent swellability of these coals is significantly reduced by drying at 373 K for one hour [16], and we have noted significant decreases in both pyridine and DMSO swellability of the coals upon 333 K drying (though the isotherm determinations at 303 K have not yet been performed following heating, to verify this hypothesis).

The comparability of isosteric heats and heats of condensation has been noted in earlier studies [10,11]. The present results also agree well with the low heats of immersion measured on a subbituminous coal (order 10^{-2} kJ/mol [17]), since such measurements would also be net of the heat of condensation of water.

3.3 DIFFERENTIAL SCANNING CALORIMETRIC MEASUREMENTS OF COAL DRYING

The hypothesis that water is held in several different forms in coal was explored by thermal means in this study. As opposed to earlier uses of DSC to examine gross heat effects of drying or to explore the freezing transition of water in coal, here a staged-temperature drying approach was utilized. In ordinary DSC scans of coal drying, there is a broad endotherm centered at temperatures above 373 K and often not completed until about 473 K [e.g. 18]. If there is interest in using such thermograms to indicate the "stability" of the water-coal interaction, great care must be exercised in these tests so as to not create a diffusional resistance within the DSC sample holder, since this could artificially create the impression of high temperature water loss (as could heat transfer limitations in the sample or mass transfer limitations on the particle level). Still, it is well established by other means that mass loss does occur at drying temperatures above 373 K[15], suggesting that some water in coal might be more tightly held than water in bulk phase.

DSC data showing a broad temperature range for moisture loss have in fact recently been interpreted in terms of a diffusion-controlled release of moisture [13]. We propose that a

distribution of energies for moisture loss may fit such data as well, and would be consistent with the picture of the existence of many different types of water-coal interactions.

Some results of measurements of thermal effects in drying of the Beulah lignite were reported earlier, and a sample of the results is shown in Fig. 4. These experiments involved heating the coal in steps from ambient to 100°C, cooling, then heating from ambient to 150°C, measuring the incremental mass loss and heat effect between 100°C and 150°C (see Fig. 4). Another sample was subjected to the same heating and cooling regimen, and then cooled again, before heating from ambient to 200°C (this is actually the experiment shown in Fig. 4). Finally, a sample was subjected to the same regimen, and then cooled and reheated and from ambient to 250°C. The reproducibility of the DSC traces, with different samples in different experiments, is very good.

It is apparent that heating a sample to any particular temperature did not result in immediate or permanent loss of all mass that could evolve below that temperature. For example, in Fig. 4, the second heating of the sample through 100°C resulted in a further detectable heat effects considerably below 100°C. This is seemingly a consequence of re-absorption of moisture that could not escape prior to cooling; this reabsorbed moisture was distributed even onto sites characterized by very low desorption temperatures. This result supports the notion of diffusion limitations as suggested above [13]. Generally, however, the maximum in desorption rate (as indicated by the maximum in the endotherm) was markedly shifted towards higher temperatures after earlier exposures to lower temperatures. This clearly argues in favor of the concept of a distribution of different energies for holding the moisture. The moisture that required higher temperatures in order to be released is presumably held in higher energy sites.

Unfortunately, these experiments cannot be cleanly interpreted at present, because of complicating factors. First, it must be recalled that this work was performed with raw coals, and thus the possible participation of mineral dehydration processes cannot be overlooked. It is doubtful that such work can be meaningfully performed with demineralized samples, since the usual acid demineralization procedure would doubtless change many of the important moisture-retention characteristics of the organic fraction of the coal. Another complication in interpreting the present DSC results comes from the fact that some CO₂ evolution occurred during nominal "drying", particularly during the higher temperature cycles. Thus some of the

endothermal behavior in the higher temperature cycles might indicate the occurrence of chemical reactions. This was further suggested by the very high enthalpies associated with mass loss during the higher temperature cycles (almost three times the latent heat of evaporation of bulk water).

The main conclusion that may be drawn from these measurements is that at temperatures below 100°C, the enthalpy of drying the lignite is not very different from the latent heat of evaporation of bulk water. Over 90% of the mass loss associated with these type of drying experiments is thus removed with an enthalpy quite close to the enthalpy of evaporation of bulk water. This is entirely consistent with the earlier conclusions drawn from examination of the isotherms, and with the conclusions of other workers [10,11]. This is not to suggest that the heat of wetting of coals by water is zero, since it is well established that the heat of wetting in water is measurable, and up to about 100 J/g for lignites [24]. It should be emphasized that such values yield isosteric heats which are at least order of magnitude less than the heat of condensation of pure bulk water.

Thus in lignites, just as in bituminous coals [11], it would appear that the interaction of water molecules with the coal substance must be energetically quite similar to the interaction of water molecules in bulk phase. Some caution must nevertheless be exercised in reaching such a conclusion. The net enthalpy change of wetting of the coal by water is what is established both by these direct thermal techniques as well as by examination of the isotherms. The net enthalpy change will likely include a significant contribution from formation of internal coal-coal noncovalent bonding interactions when the water is removed. Depending upon the magnitude of these, the measured net enthalpy change upon drying is presumably smaller than the true enthalpy change associated with removal of the water alone. One might expect the noncovalent interactions so formed to give evidence of themselves in DSC thermograms as "melting" transitions when dried coals are heated. In careful examination of thermograms, it is believed that we have found evidence of many distinct phase-transition type peaks spread over an enormous range of temperatures, and likely to have been dismissed in earlier work as "noise" in the baseline. We are reporting separately on these measurements [25]. It appears on the basis of this work, however, that there are no major heat effects (comparable in magnitude to the heat of condensation of water) detectable below pyrolysis temperatures.

Thus the net heat effect ($q_{st}-q_{cond}$) obtained from immersion experiments might be quite close to zero in that quite favorable hydrogen bonding interactions in both bulk water and the dry coal must be broken to form an equal number of equally favorable coal-water interactions. This might be the reason that Iyengar and Lahiri's estimates of the heat of immersion of lignites in water were generally too high [24]. They attempted to use reasonable estimates of the number of hydrogen bonding groups in the coal, and likewise reasonable estimates of the enthalpies of hydrogen bonding to estimate the heat of immersion of dry coals. They attempted to allow for some forms of internal coal-coal hydrogen bonding, but may not have included all important coal-coal interactions (in particular, the role of very strong nitrogen bases in the coals was not considered).

In summary, there is evidence to support earlier conclusions that there is a distribution of energies associated with how water is held in coal. All indications are, however, that the heat effects associated with the interaction of the majority of the moisture with the coal are only slightly different than the heat of condensation of pure bulk water. This might in part be due to the interaction of water with coal substitutes for equally favorable coal-coal hydrogen bonding interactions.

4.0 CONCLUSIONS

In conclusion, it has been clearly established that coals up to high volatile bituminous in rank, exhibit shrinkage upon drying which is proportional to the amount of moisture lost from the coal. The loss of moisture creates some open porosity. In the case of lignites, the porosity that is created, assuming a crude additivity of water and coal volumes, is in excellent agreement with the range of measured values of porosity in lignites. In the lignites, most of the volume occupied by the water in the coal is "created" by the swelling of the lignite structure. Thus the mechanism of capillary condensation is likely to be irrelevant to moisture retention in such systems. In the case of the bituminous coals, there must exist open porosity that is incapable of holding moisture. The holding of moisture by these coals involves the expansion of the network structure, as opposed to the filling of open porosity, just as in the lignites.

The heat effects associated with the interaction of liquid water and lignites are modest, in

comparison to the overall heat of condensation of water. The process of imbibition of moisture by coal is probably largely entropically driven, and involves the replacement of coal-coal internal hydrogen bonding interactions, by coal water interactions. The dissociation of the coal-coal hydrogen bonding interactions greatly facilitates the swelling of the coal structure, thus allowing for the accomodation of the water.

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Table 1-Ultimate Analyses of Coals Studied

<u>SAMPLE</u>	<u>C</u>	<u>H</u>	<u>N</u>	<u>S</u>	<u>ASH</u>	<u>O</u>	<u>Moisture[@]</u>	<u>Moisture*</u>
Beulah lignite ^a	65.6	3.6	1.1	0.8	11.0	17.9	29.4	29.4
Freedom lignite ^a	63.5	3.8	0.9	1.4	6.1	24.3	27.9	18.7
Glenn Harold lignite ^a	61.1	4.4	0.8	0.4	7.4	25.9	34.5	34.5
Gascoyne lignite ^a	60.9	4.2	0.6	1.4	8.2	24.7	30.7	28.9
Beulah lignite ^b	65.9	4.4	1.0	0.8	9.7	18.2	32.2	8.5
Texas lignite (PSOC1036) ^c	61.5	4.7	1.4	1.3	12.5	18.5	31.8	11.4
Belle Ayr Subbit.	69.3	4.4	1.0	0.5	10.3	14.5	30.3	20.9
Big Brown Subbit.(PSOC785) ^c	62.8	4.6	1.1	1.1	12.6	17.8	27.8	12.3
Montana Subbit.(PSOC837) ^c	57.8	4.3	0.8	0.7	11.9	24.6	17.0	13.7
Bruceton HVBit. ^d	80.4	5.3	1.6	1.0	4.6	6.7	1.7	1.5
Powhatan HVBit.	72.3	5.1	1.5	3.6	9.7	7.8	1.1	2.0

•All results on a dry weight percent basis, except moisture[@] which is reported ASTM value on an as-received, bed moist basis. Moisture* represents the actual moisture content of the samples as they were used in the present tests (note that some had dried upon storage or handling).

•Oxygen by difference.

a- Grand Forks Energy Research Center lignite sample bank.

b- Argonne National Laboratory Premium Coal Samples.

c- Pennsylvania State University Coal Sample Bank.

d- U.S. Bureau of Mines Standard Sample.

Figure 3. Sorption isotherms for water on four N.D. lignites. Open symbols-desorption; closed-adsorption. Solid curves with circles-303 K, dashed curves 323 K (V) and 333 K (Δ, Δ).

Figure 4. Differential Scanning Calorimetric curves for drying of Beulah lignite. The sample lost approximately 8% by mass of water during the preparation for the experiment, and an additional 21.25% during drying to 100°C. The mass loss in going to 150°C from 100°C was an additional 2.09%. The mass loss in going from 150°C to 200°C was not determined. See text for description of the experiment.

Figure 1. Volumetric shrinkage upon drying for coals of various rank, ranging from bituminous to lignite (see Table 1 for identification of coals). All drying experiments performed at 100°C in a vacuum oven.

Figure 2. Volumetric shrinkage of Beulah lignite upon drying at two different temperatures. Each point represents the result of a separate experiment in which the coal started with a particular moisture content, as indicated on the abscissa. The shrinkage was based upon fully drying the sample.

Figure 3. Sorption isotherms for water on four N.D. lignites. Open symbols-desorption; closed-adsorption. Solid curves with circles-303 K, dashed curves 323 K (∇) and 333 K (Δ , Δ).

Figure 4. Differential Scanning Calorimetric curves for drying of Beulah lignite. The sample lost approximately 8% by mass of water during the preparation for the experiment, and an additional 21.25% during drying to 100°C. The mass loss in going to 150°C from 100°C was an additional 2.09%. The mass loss in going from 150°C to 200°C was not determined. See text for description of the experiment.

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