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 formalizing several results relative to how moisture interacts with the structure of coal and what consequences this interaction has for practical processing of the coal. This was accomplished by combining a number of new results from solvent swelling and differential scanning calorimetry experiments, with some of the earlier reported results. The product is a paper which has been submitted for review for publication in Energy and Fuels.
present report is based in large part upon that work.

**Next Quarter Plans**

We need to develop further the new theory of coal swelling with dissociation that was developed and reported in the previous quarterly report. The model has not worked well with respect to predicting the behavior of water, perhaps because the mixing enthalpy effects are not yet well represented for that case, or perhaps because the elastic nature of coal structure is not yet well represented. In any case, significant work needs to be done on the model.

We are now in a better position to explore the elastic response of coals, as equipment has been identified that will permit new measurements to be performed. These measurements will go some way towards resolving the issues raised above.

1.0 INTRODUCTION

This introductory material repeats some material presented in an earlier quarterly, and may be skipped if the reader is already familiar with the earlier report. This study 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. In this paper are explored two issues. The first is- to what extent do coals of any rank exhibit the kind of shrinking/swelling colloidal behavior of concern? The second is -what are some consequences of practical importance, of such behavior?

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. The fact that water can be held by polar groups within the structure of coal also is well documented. 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. Another study, based on proton NMR examination of the water associated with a brown coal, reached similar conclusions. The water, crudely speaking, 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 results6,7,9), and decreases with heat treatment of the coal8. It has, however, been emphasized that the water is actually not present in discrete states, but rather in a continuous distribution of states between the bound and free states8.

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 of brown coal per unit of moisture removed have been interpreted in terms of the role of different types of moisture in coal1. The isosteric heat of moisture sorption on coals has been observed to be a function of amount of water in the coal10. The fact that hysteresis in coal moisture sorption isotherms must be determined by shrinkage and swelling effects11 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 simple12-14. There is a suggestion from recent data that the process of moisture loss may be second order13 or of apparent order between 1.3 and 2.4 relative to remaining water in the case of bound water14.

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. It must, however, be noted that there are rather strong analogies between the behavior of water in coals and behavior in other, better defined polymeric systems. For example, several of the above discussed observations have been noted also in work with cellulose15.

First, we address the question of how well the shrinking/swelling colloid model applies 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
2.1 Coals Examined

The data to be considered in this report 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 noted4. These changes will be of some importance, in the context of thermal dewatering processes.

2.2 Shrinkage Measurements

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 600μm 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%. All samples listed in Table 1, with the exception of the Wyodak and Pittsburgh No. 8 samples, were examined in these tests.

2.3 Differential Scanning Calorimetry Studies

Differential scanning calorimetric (DSC) measurements were performed on the Argonne
Premium Beulah-Zap lignite (-100 mesh) and Wyodak subbituminous (-100 mesh) samples, to explore thermally induced changes in the macromolecular structure of the coals. The technique has been described earlier. These experiments were performed in a TA Instruments 2910 DSC, by placing initially wet coal samples into aluminum DSC pans which were used in an unsealed mode. This was done by loosely fitting on the sample pans' covers, so that water or other gases could escape the pans as they were evolved. Samples were heated under a flow of nitrogen, at a heating rate of 8 K/min, to a desired temperature, and then quickly quenched.

The quenched samples from the above experiments were subjected to either of two further procedures. In the case of some samples heated to 673 K (400°C), the quenched samples were immediately re-scanned in the DSC, in a procedure designed to allow calculation of the difference spectrum from the two consecutive scans. These difference spectra have been useful for revealing irreversible physical transitions in the pre-pyrolysis zone, in higher rank samples. Other samples were quenched after only an initial heating scan to a predetermined temperature in the DSC, and then immediately weighed and subjected to solvent swelling experiments as described below. This procedure allowed tracing out the mass loss behavior as a function of temperature, and the solvent swelling data have been useful for revealing significant changes in macromolecular structure that occur in a range of temperatures of relevance for dewatering.

2.4 Solvent Swelling Experiments

These experiments have been performed as described in earlier studies. The technique involved immersion of the prepared coal samples in pure, reagent grade solvents. The measurements were performed in constant diameter glass tubes of 3 mm inner diameter and about 5 cm in length. After a sample was placed in the tube, it was centrifuged at 7500 rpm for 3 minutes in a 30 cm diameter horizontal rotor centrifuge, to permit accurate measurement of an initial dry packed height of coal. Solvent was then added to the tube, and the contents were vigorously stirred three times with a thin rod, during the first half hour of solvent immersion. This is important to prevent the coal from rapidly swelling and forming a solid plug in the tube. The coal was then allowed to swell for the desired time, and then it was again centrifuged as above, and the height of the column of coal remeasured. The ratio of the swollen height to the initial height is what is reported here as the volumetric swelling ratio.
It was often necessary during the course of the swelling measurements to change the solvents, as they became extract-laden. This was done by carefully decanting the extract-containing solvents, and replacing with fresh solvents.

3.0 RESULTS AND DISCUSSION

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:

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

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 desiccant strength (e.g. H$_2$SO$_4$, 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 2a. 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 the significance of these differences is open to question, given the uncertainty in the measurements.

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

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

In the case of the results of Figure 2a, \( a = 0.803 \), \( b = 0.900 \). Other similar tests were performed at room temperature with Gascoyne lignite (Fig. 2b, \( a = -0.182 \), \( b = 1.00 \)), with Freedom lignite (Fig. 2c, \( a = 0.230 \), \( b = 1.07 \)) and with Glenn Harold lignite (Fig. 2d, \( a = 0.386 \), \( b = 1.07 \)).
0.938). These results suggest that earlier reported shrinkage data\textsuperscript{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 relations shown above may be recast as:

\[
\frac{M_C + M_W}{V_C + V_W} = a' \frac{M_C}{V_W - V_P} + (a' + b) \frac{M_W}{V_W - V_P}
\]

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. Note that in deriving this result, it was assumed that the fractional volumetric shrinkage is given by \((V_W - V_P)/(V_C + V_W)\), where it is assumed that in the wet state there is no open porosity (it is filled with water). It should also be noted that in this representation, the numerical value of \(b\) is as above, and \(a' = a/100\) as a result of converting from a percentage to fractional basis. 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\textsuperscript{4}. This leads to the conclusion that:

\[
\frac{1}{1.2} = 0.833 \text{ cc/g} = \frac{1}{b \cdot V_P/(bM_W)}
\]

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:

\[
V_P/M_C = \frac{M_W}{M_C} (1 - 0.833 b) \text{ cc/g}
\]

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\textsuperscript{20}.

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, where real measured values are of order 0.1 g/cc\textsuperscript{20}). The conclusion is that the porosity had to already be present, rather than being created by moisture loss, and the assumption made in deriving (3), that there is no open porosity in the wet coal, is not appropriate for these coals. This is obvious if one considers 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 0.1 cc/g. Alternatively, if one were to merely fill existing porosity with water, the equilibrium moisture content of bituminous coals should be closer to 10% than 1%. This is interesting, insofar as these coals do fit the correlation for shrinkage upon drying quite well. This seemingly implies that little of the moisture is held in what is, in the dry state, measured as open porosity. Since a significant fraction of the porosity is often macroporosity, which should be fillable by ordinary capillary processes, the implication is that the surfaces of the pores are highly hydrophobic.

What the above results imply is that the lower rank coals will behave like ordinary colloidal gels. They cannot completely collapse to a zero porosity solid upon drying, but do so to a significant extent. The higher rank coals also show distinctly colloidal shrinkage behavior, but have in coalification collapsed in a manner in which open porosity has already been created. The fact that the structure of the coals in all cases significantly expands to accommodate 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. Issues related to the thermodynamics of coal swelling have been reviewed elsewhere.

3.2 Solvent Swelling Studies

The rather significant shrinkage that low rank coals undergo as they dry has already been reported to have some important practical implications. For example, it was seen that the more severe the drying of a lignite, the more its porosity would collapse, and the lower would be its apparent surface area. The effects on the transport of species through the coal might also be expected to be influenced by the collapse of the structure. In polymers, it has been observed that "aging" polystyrene under vacuum reduces both the apparent equilibrium uptake and the kinetics of uptake of n-hexane by the polymer. The evacuation of the polymer results in the consolidation of the glassy polymer by slow relaxation processes. Similar processes might be expected to play a role in coals.
The removal of water from coal might be expected to have another important role, with respect to diffusional transport in coals. Again, it is well established in the polymer literature that polymers that are significantly hydrophilic (i.e. they can pick up more than 20% moisture) always exhibit increasing diffusivity of gases as the relative humidity of the gas in contact with the polymer increases\textsuperscript{23}. With polymers that are only slightly hydrophilic (less than 1% water uptake at equilibrium), there is little effect of moisture on diffusivity. Thus coals span the full range of moisture uptake, and the expectation is that lignites would exhibit enhanced transport rates in the wet state. It has already been noted that solvent pre-swelling of bituminous coals (with solvents other than water) does not affect diffusional transport rates very much\textsuperscript{24}. We will show below that this may be true in certain cases, but is not always true.

The effect of moisture on the equilibrium solvent swelling ratio of a coal in a good swelling solvent is considered first. The data of Figure 3 show important features, in this case for Wyodak subbituminous coal. In this figure, the top panel presents the DSC difference spectra for three consecutive scans of the same sample. As discussed above, if there are no irreversible changes occurring in a sample, then a flat line near zero should result. This is seen to be roughly the case in the difference between second and third scans. The dominant feature in the differences with respect to the first scan is the water evaporation endotherm centered at around 373 K. The lowest panel of the figure shows the loss of mass that occurs during heating to the indicated temperature. The fact that the majority of the water does not come off until a temperature above 373 K is attained should be considered in view of the fact that the water loss is a kinetically controlled process, as noted above. The point shown at 373 K refers to a sample heated to that temperature, and then immediately quenched, so there is effectively no soak time at 373 K. By the time the process is taken up to 423 K, the more "normal" moisture loss value is obtained. It is significant that the endotherm itself extends up to 473 K, suggesting that the removal of the last "moisture" is quite slow, and not characterized by a clean endpoint. Difficulties associated with defining an endpoint in moisture determinations have, of course, been noted many times\textsuperscript{25-27}.

In this case, at the particular heating rate used here (8 K/min), the moisture is lost between 373 K and 423 K. The middle panel shows the effect of the heating process on the subsequent swellability of the coal in pyridine and tetrahydrofuran (THF). Again, the swelling tests were performed on samples that had been cooled immediately upon attaining the indicated temperatures;
solvent exposure occurred only at room temperature. The pyridine swellability shows a dramatic apparent increase in the range between 373 K and 423 K. This increase is an artifact due to the fact that water, a swelling agent, is being removed from the structure, and the structure responds by collapsing. For the amount of loss of moisture in heating to 423 K, the correlation given in section 3.1 would predict a 23% shrinkage in structure. If the swelling ratio of the raw coal (1.9) is multiplied by the extra swelling already corresponding to the water present, the result is a swelling ratio of about 2.3, which is in fair agreement with the measured value of roughly 2.4.

A similar “correction” to a dry basis is apparently not needed in the case of the THF swelling data. The THF is a significantly weaker solvent for the coal than is pyridine; even though THF and pyridine have very similar molar volumes, the coal swells much less in the THF, and this shows that fewer moles of THF are imbibed by the coal. The most likely reason that THF does not show a step increase in swelling ratio between 373 K and 423 K is that as the coal loses moisture in that temperature range, there are formed new non-covalent interactions in the coal, involving sites that are strongly polar or hydrogen bonding in nature. The THF is apparently unable to solvate (break) as many of these new interactions as is pyridine, which is a strong base. These non-covalent interactions involving different parts of the coal structure can be globally characterized as electron donor-acceptor interactions, and will span a broad spectrum of interaction strengths. It is the strength of the solvent as an electron donor that has been hypothesized to govern the efficacy of coal swelling solvents28.

Figure 4 shows the same kinds of data as in Figure 3, but for the Argonne Premium Beulah-Zap lignite sample. The behavior discussed in connection with Figure 3 is also evident here. Removal of water above 100°C again results in a shrinkage of the base against which the pyridine swelling is compared. In this case the untreated room temperature swelling ratio of about 1.7 must be multiplied by a factor of 1.26 (measured shrinkage) to yield a final swelling ratio of about 2.1, in quite good agreement with the measured value at long times. Once again, the correction is not evident from the results for THF swelling, since the THF cannot resolvate the newly formed intracoal interactions.

What is evident in Figure 4 that was not evident in Figure 3 is the fact that the kinetics of swelling are also significantly affected by the drying process. For example, in the case of the pyridine swelling, there is an abrupt decrease in the short-time swellability of the coal, when the
moisture is removed. This alone could lead to a mistaken conclusion about the possibility of very severe low temperature crosslinking, if swelling is not followed long enough. At long times, however, it is clear that the behavior noted with Wyodak coal is followed. The decrease in swelling kinetics is also quite evident in the results for THF.

There is little evidence of the kinetics of swelling changing much between 423 K and 623 K, even though the equilibrium swellability in pyridine continually decreases throughout this range of temperatures. This seemingly implies that crosslinking, which shows itself as a decrease in equilibrium swellability, does not much influence the kinetics of swelling of the coal. Generally, in rubbery polymers, the rate of diffusion decreases with an increase in degree of crosslinking. In this kind of a glassy system in which the diffusing solvent serves to relax the structure, it is relaxation, rather than diffusion, that determines the rate of swelling. This rate would also be expected to be affected by crosslink density, but it is unclear by how much.

Thus we see the effect of water as a plasticizing solvent for coal, enhancing transport of solvent through the coal by helping to pre-relax the structure, and thus enhancing kinetics. There appears to be an analogy with the well-known effect of water in polymer systems, in which the effect is due to enhanced transport. Since the pyridine is a stronger electron donor than water, it will probably disrupt coal-coal non-covalent interactions that water cannot. The fact that the structure is initially more loose allows the pyridine easy access to more parts of the structure than it would otherwise have initially.

The phenomenon has been explored in more detail in two other coals. Another lignite has been subjected to detailed examination of the kinetics of swelling in pyridine, as a function of the moisture content of the lignite. The results are shown in Figure 5. One curve shows the swelling behavior of a sample of dried lignite (drying at 373 K) as a function of time. This curve shows that equilibrium is achieved within 3000 seconds (a bit less than an hour). This behavior is more like that of the easily swelled Wyodak of Fig. 3 than the slowly swelling lignite of Fig. 4, and points out the quite significant coal-to-coal variations in swelling kinetics.

Also shown in Fig. 5 are two curves for the sample of lignite used in an air-dried state (9 % wt. residual moisture). One curve shows actual experimental data. The second curve shows the experimental points corrected for the fact that in the wet state the coal is water swollen; the correction is of precisely the same nature as discussed above in connection with Figs. 3 and 4.
Again, the correction brings the final equilibrium swelling values relative to the dry state into excellent agreement with the actual measurements relative to the dry state. The comparison of the kinetics of swelling in a wet state to those in a dry state again unequivocally establish the role of water in enhancing the kinetics of solvent uptake by the coal.

The effects are not limited to coals of low rank. Figure 6 shows results for a high volatile bituminous coal. The results need no correction for preswelling by water, in this case, because the bituminous coal contains only about 1.7% by mass moisture to begin with, and is thus preswollen to an extent of less than about 2% by water. The comparison of the rates of swelling in the wet and dry states clearly shows that even in this high rank coal, water enhances the rate of solvent uptake to a significant degree. Note that this coal reached equilibrium uptake in almost an order of magnitude shorter time than did the lignite of Figure 5. The rank dependence of solvent swelling rates has been noted previously\textsuperscript{19, 29,30}. Thus an earlier observation that the rate of uptake of maleic anhydride by bituminous coals is independent of the degree of swelling of the coals\textsuperscript{24} cannot be used to infer in general that preswelling of coals is unimportant to rates of uptake of penetr.

We have performed experiments in which the effects of different levels of moisture content were created in a single coal, and the effects upon solvent uptake kinetics were determined. The experiments involved drying a Deulah lignite (not the Argonne sample, but similar in nature) for three hours at 373 K, in vacuum, and then re-exposing the samples to various levels of relative humidity at 298 K. The samples regained different levels of moisture. Then the samples were then immersed in pyridine at 308 K, and the kinetics of swelling were tracked. The results of such tests are shown in Figure 7. This figure shows the time required to achieve 30% and 50% of equilibrium swelling, in experiments similar to those shown in Figures 5 and 6. The choice to represent the data in terms of these percentages of swelling is an arbitrary, but convenient, manner in which to represent the kinetics of swelling. The kinetics do not normally follow simple kinetic expressions, but are often somewhere between Fickian and “Case II” (relaxation controlled) in nature\textsuperscript{19,31}. The data of Figure 7 show the systematic variation of kinetics with moisture content. The greater the moisture content, the faster the further uptake of solvent by the lignite. More precisely, the more swollen the coal is by water, the less time is required to reach any additional extent of swelling in pyridine. The fact that the curves are smoothly varying over a broad range of
moisture contents shows that there is not a particular moisture level at which the effect is seen to suddenly manifest itself.

The data of Figure 7 also demonstrate clearly that the slowing of solvent uptake with moisture loss is not an artifact caused by an irreversible "collapse" or "tightening" of the lignite structure upon drying. In this case, all samples had been subjected to equally severe drying conditions, prior to rehydration. The effect on solvent uptake kinetics is clearly related to how much moisture the coal has in it at that moment.

The same types of samples as used in obtaining the data of Figure 7 were subjected to tests in which the samples were swollen in pyridine at temperatures ranging from 298 K to 320 K. From these kinetic measurements, activation energies were calculated for the swelling process. These were obtained by assuming that the swelling was governed by a "Case II" type of mechanism, and thus a linear relationship between solvent uptake and time, during the early stages of swelling. Typical data are shown in Figure 8. The process, as noted earlier, was actually not cleanly Case II in nature, but for the purposes of this analysis, was close enough to allow the values of the swelling rate constant to be estimated. These values of rate constant are shown in Figure 9. It is apparent that on this basis, the activation energy for the swelling process is fairly constant, at about 73 kJ/mol, irrespective of the moisture content of the sample. Thus the basic relaxation mechanisms that determine the swelling rate are not changed by the presence of moisture. The effect of moisture is to apparently provide greater access to the structure of the coal.

We had earlier drawn a tentative conclusion that the activation energy of the relaxation process varies slightly with the moisture content of the coal. That conclusion was based upon a somewhat cruder kinetic analysis, and we believe that it neglected the importance of non-Case II behavior, by examining the kinetics over a range too broad to be well characterized by linear behavior. Nevertheless, all of the values earlier reported were obviously quite close to the value reported here (within 10-15%). Based upon our analysis here, we believe there is no evidence of a systematic variation in the activation energy of the swelling process with moisture content.

It was noted in connection with Figures 3 and 4 that heat treatment tends to crosslink the structure of the coals, as evidenced by the continual decrease in pyridine swelling ratio at temperatures in excess of 423 K. This low temperature crosslinking has been noted in many other studies as well. It was surprising to us that the increase in crosslinking did not results in a more notable effect on solvent uptake kinetics. To address this point further, other data are
considered. These data were taken from experiments in which the samples were heat-soaked for extended periods of time, rather than being quickly heated to temperature and quenched, as in the case of the samples of Figures 3 and 4. Typical results are shown in Figure 10.

Figure 10 shows the uptake curves for pyridine in samples of dried Beulah lignite. These samples were prepared from the first lignite in Table 1, ground to 150-212 μm particle size in all cases. The samples were all first dried for 3 hours under vacuum, at 373 K, and then subjected to an additional heating of one hour at the temperature indicated. The pyridine swelling results were obtained on the cooled coal (chars) at a temperature of 309 K. The swelling temperature made little difference in the results (298 to 320 K were examined). The full temporal history is not shown, because the equilibration was quite slow towards the end.

There is a clear trend towards slower uptake kinetics, the more highly heat-treated the sample. The samples all lost a significant amount of mass in the period of heating above 373 K. The sample heated at 473 K lost an additional 4.3%, that heated at 593 K lost an additional 12.3%, and that heated at 668 K lost an additional 21.2%, all relative to the 373 K dry basis. Indicated on the curves of Figure 10 are the final equilibrium swelling values attained in these experiments. The fact that the pyridine swelling ratio declined significantly at a time when chemical reactions leading to mass loss were proceeding strongly suggests that crosslinking reactions were occurring in the lignite. The change in equilibrium swellability is measurable, but not dramatic. The effect on the kinetics of solvent uptake is significant.

The effect of heat treatment is likely to be associated with the crosslinking involving oxygen-containing functional groups in low rank coals. This is supported by the fact that heat treatment appears to have the opposite effect in the case of a higher rank coal, the Pittsburgh No. 8 high volatile bituminous coal. Results are shown in Figure 11 for the dried coal, and a sample heat treated at a rate of 8 K/min to 668 K, and then quenched. The equilibrium swelling ratios of both samples are insignificantly different (2.14 and 2.18, for the untreated and heat-treated samples, respectively). Thus there appears to be no covalent crosslinking during heat treatment, even though there is an effect on swelling kinetics.

We have earlier shown that there is a thermally induced pre-pyrolysis physical relaxation of structure in the Pittsburgh No. 8 coal (at around 540-570 K), that enhances its swellability in weak solvents. The present results show that if the kinetics of swelling are carefully
examined, the effect of the relaxation can also be seen with good solvents such as pyridine. The difference between the low rank coals and high rank coals, noted here and in other work, has historically been attributed to the role of low-temperature crosslinking processes that occur in the low rank coals, but not in the high rank coals.\textsuperscript{33-36} It should also be remarked that comparison of the timescales of Figures 10 and 11 again points up the enormous range of kinetics observable with different types of coals; comparable extents of swelling take an order of magnitude longer in the low rank coal. (Swelling of the Wyodak subbituminous coal is faster even than swelling of the Pittsburgh No. 8 coal, so there is no consistent trend with rank).

There can no longer be much doubt as to the generality of the conclusion that low temperature heating induces crosslinking reactions in low rank coals. What comes as somewhat of a surprise is the fact that the effect is seen at temperatures as low as are often used to "dry" the coals. This is emphasized by the data of Table 2, on four different North Dakota lignites. Considering first the top three rows of the table, there is clearly a trend towards higher apparent swelling ratio, as moisture is removed more efficiently. This is the same effect as has been discussed at length above. What came as more of a surprise is the comparison of the third and fourth lines of Table 2, in which drying at 373 K gives higher swelling ratios than for samples dried at 300K in a zero relative humidity environment. Direct measurement of the moisture loss by the two drying techniques showed at most an additional 2\% loss of moisture, in the higher temperature case. This suggests, in terms of our earlier shrinkage experiments, that the base for calculating swelling ratios should not be significantly different in these two cases, thus the magnitude of the difference came as a surprise.

We now believe that in addition to promoting a bit more moisture loss, the exposure of samples to elevated temperatures promotes further collapse (densification) of the structure, beyond that associated with the removal of moisture at 300K. The collapse is at least in part reversible, and gives rise to the higher apparent swelling ratio, since the initial volume is smaller. This is consistent with our earlier observation that the nitrogen BET surface areas of these lignites always decrease when they are dried at 373 K, rather than at 300 K.\textsuperscript{4}

The last four rows of Table 2 show the effect of heating the samples dried for 30 days at 300 K. There is always a significant decrease in equilibrium swelling ratio, even when heating is carried out at only 373 K. Thus great care must be exercised in any practical applications in which
crosslinking of low rank coals might be deleterious (e.g., liquefaction); even drying procedures can significantly influence the macromolecular structure of the lignite.

These data make clear the importance of sample temperature history on solvent swellability (and thus macromolecular structure), but leave open questions as to mechanism. The samples first dried at 300 K and then exposed to 373 K are in three cases apparently significantly more highly crosslinked than the samples heated directly to 373 K. Since the heating after 300 K was always performed in an inert atmosphere, the crosslinking is not an artifact of oxidation during the high temperature step. The samples could, however, have been somewhat oxidized during the drying at 300 K, since no attempt was made to exclude oxygen during the long period of storage, even though the container was tightly sealed for most of that time. This leaves open the possibility of crosslinking induced by oxygen picked up during low temperature storage. On the other hand, the crosslinking processes might just be more efficient, if the heating is begun from a dried state, and oxidation plays no role. Further work is required on this question.

4.0 REFERENCES

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Table 1—Ultimate Analyses of Coals Studied

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>ASH</th>
<th>O</th>
<th>Moisture@</th>
<th>Moisture*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beulah lignite</td>
<td>65.6</td>
<td>3.6</td>
<td>1.1</td>
<td>0.8</td>
<td>11.0</td>
<td>17.9</td>
<td>29.4</td>
<td>29.4</td>
</tr>
<tr>
<td>Freedom lignite&lt;sup&gt;a&lt;/sup&gt;</td>
<td>63.5</td>
<td>3.8</td>
<td>0.9</td>
<td>1.4</td>
<td>6.1</td>
<td>24.3</td>
<td>27.9</td>
<td>18.7</td>
</tr>
<tr>
<td>Glenn Harold lignite&lt;sup&gt;a&lt;/sup&gt;</td>
<td>61.1</td>
<td>4.4</td>
<td>0.8</td>
<td>0.4</td>
<td>7.4</td>
<td>25.9</td>
<td>34.5</td>
<td>34.5</td>
</tr>
<tr>
<td>Gascoyne lignite&lt;sup&gt;a&lt;/sup&gt;</td>
<td>60.9</td>
<td>4.2</td>
<td>0.5</td>
<td>1.4</td>
<td>8.2</td>
<td>24.7</td>
<td>30.7</td>
<td>28.9</td>
</tr>
<tr>
<td>Beulah-Zap lignite&lt;sup&gt;b&lt;/sup&gt;</td>
<td>65.9</td>
<td>4.4</td>
<td>1.0</td>
<td>0.8</td>
<td>9.7</td>
<td>18.2</td>
<td>32.2</td>
<td>8.5</td>
</tr>
<tr>
<td>Texas lignite (PSOC1036)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>61.5</td>
<td>4.7</td>
<td>1.4</td>
<td>1.3</td>
<td>12.5</td>
<td>18.5</td>
<td>31.8</td>
<td>11.4</td>
</tr>
<tr>
<td>Belle Ayr Subbit.</td>
<td>69.3</td>
<td>4.4</td>
<td>1.0</td>
<td>0.5</td>
<td>10.3</td>
<td>14.5</td>
<td>30.3</td>
<td>20.9</td>
</tr>
<tr>
<td>Big Brown Subb. (PSOC785)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>62.8</td>
<td>4.6</td>
<td>1.1</td>
<td>1.1</td>
<td>12.6</td>
<td>17.8</td>
<td>27.8</td>
<td>12.3</td>
</tr>
<tr>
<td>Montana Subbit. (PSOC837)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>57.8</td>
<td>4.3</td>
<td>0.8</td>
<td>0.7</td>
<td>11.9</td>
<td>24.6</td>
<td>17.0</td>
<td>13.7</td>
</tr>
<tr>
<td>Wildcat Subbit. (PSOC636)&lt;sup&gt;c&lt;/sup&gt;</td>
<td>60.9</td>
<td>4.9</td>
<td>1.1</td>
<td>2.5</td>
<td>16.0</td>
<td>14.6</td>
<td>30.7</td>
<td>19.6</td>
</tr>
<tr>
<td>Wyodak Subbituminous&lt;sup&gt;b&lt;/sup&gt;</td>
<td>68.4</td>
<td>4.9</td>
<td>1.0</td>
<td>0.6</td>
<td>8.8</td>
<td>16.3</td>
<td>28.1</td>
<td>28.1</td>
</tr>
<tr>
<td>Pittsburgh No. 8 HVBt.&lt;sup&gt;b&lt;/sup&gt;</td>
<td>74.2</td>
<td>4.1</td>
<td>1.4</td>
<td>2.3</td>
<td>13.2</td>
<td>4.8</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Bruceton HVBt.&lt;sup&gt;d&lt;/sup&gt;</td>
<td>80.4</td>
<td>5.3</td>
<td>1.6</td>
<td>1.0</td>
<td>4.6</td>
<td>6.7</td>
<td>1.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Powhatan HVBt.</td>
<td>72.3</td>
<td>5.1</td>
<td>1.5</td>
<td>3.6</td>
<td>9.7</td>
<td>7.8</td>
<td>1.1</td>
<td>2.0</td>
</tr>
</tbody>
</table>

• 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.

<sup>a</sup>- Grand Forks Energy Research Center lignite sample bank.
<sup>b</sup>- Argonne National Laboratory Premium Coal Samples<sup>16</sup>.
<sup>c</sup>- Pennsylvania State University Coal Sample Bank.
<sup>d</sup>- U.S. Bureau of Mines Standard Sample.
Table 2- Effect of Drying and Thermal Treatments on Pyridine Swelling of Lignites

<table>
<thead>
<tr>
<th>Condition</th>
<th>Beulah</th>
<th>Freedom</th>
<th>Gascoyne</th>
<th>Glenn Harold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>1.48</td>
<td>1.62</td>
<td>1.33</td>
<td>1.60</td>
</tr>
<tr>
<td>0% R.H., 300K, 24hrs</td>
<td>2.20</td>
<td>2.01</td>
<td>1.90</td>
<td>2.10</td>
</tr>
<tr>
<td>0% R.H., 300K, 30 days</td>
<td>2.22</td>
<td>2.06</td>
<td>2.10</td>
<td>2.14</td>
</tr>
<tr>
<td>Wet, dried at 373K, 1 hr</td>
<td>2.34</td>
<td>2.50</td>
<td>2.05</td>
<td>2.47</td>
</tr>
<tr>
<td>Dry, then 373K, 1 hr</td>
<td>2.00</td>
<td>1.70</td>
<td>1.68</td>
<td>1.81</td>
</tr>
<tr>
<td>&quot; then 473K, 1 hr</td>
<td>1.43</td>
<td>1.66</td>
<td>1.54</td>
<td>1.75</td>
</tr>
<tr>
<td>&quot; then 573K, 1 hr</td>
<td>1.22</td>
<td>1.45</td>
<td>1.50</td>
<td>1.50</td>
</tr>
<tr>
<td>&quot; then 573K, 2 hr</td>
<td>1.14</td>
<td>1.30</td>
<td>1.42</td>
<td>1.45</td>
</tr>
</tbody>
</table>

- All values are volumetric swelling ratios
- 0% R.H. refers to drying over concentrated sulfuric acid, a 0% relative humidity environment. Samples marked "dry" were initially dried in this manner at room temperature, for periods of at least 30 days, prior to thermal treatment.
Figure 1. Volumetric shrinkage upon drying for coals of various rank, ranging from bituminous to lignite (see Table 1 for coals; includes all except the Wyodak and Pittsburgh No. 8). All drying experiments performed in a 373 K vacuum oven.
Figure 2a. Volumetric shrinkage of Beulah lignite upon drying at two different temperatures. Each point represents the result of a separate experiment in which the lignite started with a particular moisture content, as indicated on the abscissa. The shrinkage value reported is that for drying from the starting moisture content to a fully dry state.
Figure 2b. Volumetric shrinkage of Gascoyne lignite upon drying at 298 K. Each point represents the result of a separate experiment in which the lignite started with a particular moisture content, as indicated on the abscissa. The shrinkage value reported is that for drying from the starting moisture content to a fully dry state.
Figure 2c. Volumetric shrinkage of Freedom lignite upon drying at 298 K. Each point represents the result of a separate experiment in which the lignite started with a particular moisture content, as indicated on the abscissa. The shrinkage value reported is that for drying from the starting moisture content to a fully dry state.
Figure 2d. Volumetric shrinkage of Glenn Harold lignite upon drying at 298 K. Each point represents the result of a separate experiment in which the lignite started with a particular moisture content, as indicated on the abscissa. The shrinkage value reported is that for drying from the starting moisture content to a fully dry state.
Figure 3. a) Difference DSC, b) solvent swelling and c) mass loss of Wyodak subbituminous coal as a function of temperature. The samples were all heated from an as-received state at a rate of 8 K/min. In the case of the solvent swelling experiments and the mass loss determinations, the samples were quickly quenched to room temperature from the indicated temperatures, prior to the measurements.
Figure 4. a) Difference DSC, b) solvent swelling in pyridine, c) solvent swelling in THF, and d) mass loss of Beulah-Zap lignite as a function of temperature. The samples were all heated from an as-received state at a rate of 8 K/min. In the case of the solvent swelling experiments and the mass loss determinations, the samples were quickly quenched to room temperature from the indicated temperatures, prior to measurements.
Figure 5. Volumetric swelling ratios in pyridine, of Texas lignite at 298 K. Triangles are for dried lignite, with no moisture content. The open squares are the raw data for air-dried lignite of 9% moisture content. The solid squares show the corrected data for the 9% moisture lignite (see text). All results are for 212-300 μm particles. The dry sample was prepared by vacuum drying at 373 K for three hours.
Figure 6. Volumetric swelling ratios in pyridine of Powhatan No. 5 high volatile bituminous coal, at 298 K. The solid points are for wet coal (1.7% moisture) and the open points are for dried coal. The dry sample was prepared by vacuum drying for three hours at 373 K.
Figure 7. Swelling behavior of Beulah lignite in pyridine at 308 K. The ordinate shows the time required to achieve 30% or 50% of the final extent of swelling, as a function of the initial moisture content of the samples. All samples had been initially dried for three hours at 373 K, prior to rehydration to the indicated moisture contents.
Figure 8. The swelling behavior in pyridine at 298 K, of Beulah lignite samples of three different moisture contents. Triangles, 11.2% moisture; open squares, 6.6% moisture; solid squares, zero moisture content.
Figure 9. Swelling rate of Beulah lignite in pyridine, as a function of moisture content and temperature of swelling. Triangles, 11.2% moisture; open squares, 6.6% moisture; open squares, zero moisture content.
Figure 10. The effect of heat treatment on the swelling kinetics of Beulah lignite in pyridine at 309 K. The values indicated next to each curve are the final equilibrium swelling ratios achieved at long times. All samples were sieved to 150-212 μm particle size range, and predried at 373 K under vacuum. Then each sample was subjected to one additional hour at the following temperatures—solid squares, 373 K only; open squares, 473 K; triangles, 593 K; diamonds, 668 K.
Figure 11. The effect of heat treatment on the swelling kinetics of Pittsburgh No. 8 coal in pyridine at 297 K. Open squares- dried coal; solid squares, coal heat-treated to 668 K.
END

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