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)
Y. OTAKE AND S.C. DEEVI (CONTRIBUTIONS TO REPORT)

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

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 report consists of a manuscript prepared on the topic of elastic response of coals, as studied by mercury porosimetry. It illustrates some important points about the structure of coals, and what state the structures might be in, during various types of analyses.
Next Quarter Plans

The project will be brought to a formal close, as far as experimental studies are concerned. There will be no further experimental work, as there are no further funds to pay for student work on the project. Attention will be turned to the analysis of a large amount of unanalyzed data.
INTRODUCTION

Mercury porosimetry is a widely used technique for examining the pore structure of solids. The method has found frequent application in examination of coals. Recently, questions have been raised about the interpretation of surface area and porosity measurements on raw coals, since they do not have a rigid pore structure, but rather behave as a colloidal gel, with water as the solvent. The "porosity" which is determined by mercury porosimetry and gas adsorption techniques is generally of interest with respect to rates transport of chemical species through the coal during high temperature processing. Such porosity values might not be a quantitatively reliable basis for calculating transport rates, however, because the structure of the coal gel can be profoundly altered by heating and/or solvent exposure well before any reactions take place (the same is not the case for a highly heat-treated char which has a much more rigid structure). Nevertheless, mercury porosimetry is still widely applied to raw coals. Some aspects of the measurements, and what they can reveal about the macromolecular structure of coals, will be examined here.

In the classical application of the mercury porosimetry technique, the volume of mercury that can be forced into the pores of a solid in any particular range of pressure gives an indication of the porosity in a certain range of sizes. When the technique is applied to coals, quantitative interpretation of the results presents several difficulties. One problem is associated with the fact that the "pores" are not truly cylindrical, but rather slit-shaped. Another is the fact that the apparent increase in mercury uptake by coal at higher pressures (>10 MPa) is actually due to the compression of coal structure. Because of this, the application of mercury porosimetry to pore characterization of coals has usually involved corrections for this compression. The need for the compressibility correction has normally been operationally defined by a region in which mercury uptake curves are more or less linear in applied pressure.

The compressibility of a solid is formally defined by:

\[ \kappa = -(1/V)(\partial V/\partial P)_T \]  

where \( V \) is sample volume and \( P \) is pressure. This quantity is the reciprocal of the so-called "bulk
modulus”, B. As will be discussed below, these quantities are related to other common mechanical properties of the coal.

**EXPERIMENTAL**

The coals that have been examined in this part of the study include two Argonne Premium Coal Samples\(^8\) - Illinois No. 6 and Pittsburgh No. 8. Additionally, a series of four North Dakota lignites has been examined, as well as a sample of Powhatan No. 5 bituminous coal. The analyses of these coals are presented in Table 1. Samples that were studied were generally fairly fine powders, -20 +100 mesh in size.

Mercury “porosimetry” (compression and decompression) was carried out using a standard Quantachrome Instruments mercury porosimeter. This instrument can be used to scan mercury pressures up to \(227\) Mpa (33,000 psia). Normally the instrument scans at 45.5 MPa/min. In some tests, the scans were deliberately interrupted and samples held at a constant pressure. In a departure from “normal” practice, here both compression and decompression cycles were examined. The terminology “uptake volume” will be used to denote the measured decrease in mercury volume with increase in applied pressure. It is recognized that this term does not necessarily reflect the actual physics of the process, in that actual penetration of pores is not the main process of interest. No interpretation of the low pressure part of the intrusion curves will be presented, since the actual porosity information is of no interest here.

**RESULTS AND DISCUSSION**

Figures 1 through 3 show typical results from mercury “porosimetry”. The zero mercury uptake reference point was defined at an initial applied mercury pressure of 0.4 MPa.

Figure 1 shows the effect of sample drying on the results that are obtained. The dried lignite samples (whether dried at room temperature or at 373 K) show a higher uptake of mercury at low pressures. Upon drying, the lignite “gel” structure collapses, but significant amounts of mesoporosity and macroporosity survive and are, in fact, created by the drying. Overall, the Glenn Harold lignite structure shrinks by almost 40\% by volume upon drying, so the changes in the porous structure are profound, and it is presumably not a simple matter of removing water from
pre-existing pores that results in the greater mercury uptake. The other notable feature in these results is that there is always a hysteresis evident in the compression-decompression cycles. This hysteresis was also noted in all other results obtained in this study.

In this study, the main focus is on the high pressure, fairly rectilinear portions of the compression curves. In the case of the Glenn Harold lignite, this region is seen to begin at almost 50 MPa. In as-received Pittsburgh No. 8 coal (Fig. 2), the linear portion of the curve obtains at about 100 MPa, whereas in the as-received Powhatan No. 5 coal (Fig. 3), it was also seen above 50 MPa. There was a fair deal of variability observed in this onset point. As noted above, it has been customary to associate the uptake of mercury in this high pressure range with the compression of the sample. A blank run ascertained that the compressibility of the measurement apparatus itself was negligible compared to that exhibited by the sample in this range.

As a thermodynamic property, the bulk compressibility would not be expected to be path-dependent. Thus the observed hysteresis, such as displayed in Figures 1 through 3 and seen in all other experiments we performed, must be viewed as inconsistent with simple interpretations of the high pressure behavior in terms of simple reversible compressibility.

Hysteresis behavior is not uncommon in mercury porosimetry work. A classical explanation of this sort of behavior is the so-called “ink-bottle” model. According to this model, pores have narrow necks that preclude their filling until high pressures, but have wide bodies, which prevents their emptying until low pressures. Alternatively, hysteresis has been explained by differences in advancing and receding mercury contact angles in the solid.

Thus there is a fundamental inconsistency not only between the usual, simple interpretation of the high pressure compression behavior in coals and the existence of hysteresis behavior, but also between the generally accepted models of hysteresis, which are based upon pore penetration, and the conclusion that pore penetration is not significant in determining uptake at high pressures. While we have serious reservations about the value of quantitative measurements of the pore structures of raw coals and thus do not seek to clarify these issues for that purpose, we do believe that these results help illustrate some interesting features of coal network structure behavior.

The nature of the apparent hysteresis in the pressure range from 20 MPa to 227 MPa was further examined by various techniques. A series of several consecutive compressions and
decompressions were performed on a sample of Illinois No. 6 coal, and the results are shown in Figure 4. It should be noted that in this case, the starting sample was "wet" (as received) and so there is little penetration of "porosity" evident in the first cycle. Again, this is of little concern here, where porosity was not the main issue of interest. The same decompression cycle was always traced out. Such behavior has also been observed in a very different kind of materials (e.g. alumina-silica gel\(^1\)). Also, after the first compression-decompression cycle, all subsequent compression-decompression cycles were essentially identical, implying that the process had become reversible.

The fact that pre-drying of a sample does not alter the above conclusions is borne out by the results of Figure 5, obtained on a pyridine pre-extracted and pre-dried sample. Here, a more "normal" pore penetration behavior is seen, together with irreversible uptake. Again, all decompression curves are coincident, and all subsequent compression curves are likewise coincident.

Since in the undried sample of Figure 4, the first compression curve was not parallel to the second and subsequent compression curves not only in the low pressure range, but also in the linear 20 to 227 MPa range, this suggests that there are irreversible changes occurring in this range of pressure. These might have little to do with actual pore filling, and could even involve loss of some of the moisture from the sample. Since this was not a key aspect of the present study, no attempts were made to verify this hypothesis.

In Figure 5, all uptake curves are coincident above about 80 MPa. In classical porosimetry, the difference between the first and all subsequent compression cycles is often attributed to an irreversible uptake of mercury in the pores of the coal. The fact that the uptake curves for the first and subsequent cycles coincide in the high pressure range is not at variance with this. The classical interpretation would be that the pores were all irreversibly filled during the first cycle, and the high pressure behavior is attributable to the reversible compression of the sample. There is, however, also the possibility of permanent damage to the pore structure, as has been established to occur in other materials\(^{1,9}\). There is no way to easily distinguish from these results whether there has been irreversible filling of pores or actual physical damage. Again, the classical interpretation of the high
pressure behavior disregards the existence of the hysteresis loop.

Since there is a high degree of reversibility shown on repeated cycles, the major high pressure-induced changes that occur on the second and third compression cycles, and give rise to hysteresis, are not due to any permanent alterations in the gross macroscopic structure of coals (i.e. collapse of macroscopic voids). Also, as has been noted before, the relative linearity of the uptake with pressure in the high pressure region (in virtually all cases) seems to argue in favor of the uptake involving compression rather than true pore penetration. It is more likely that reversible changes in structure are being caused on a molecular level. The coal material itself can be reversibly pushed into a tighter packing arrangement by the applied pressure. The resulting hysteresis behavior could be attributable to the slow kinetics of relaxation of some parts of the structure, upon decompression. It might even be that a certain critical driving force, that depends upon external pressure, is needed in order for relaxation to occur.

We have recently presented evidence for thermally- or solvent-assisted relaxation of raw coals. It appears that coal structure is initially at equilibrium relative to its geological conditions of formation, but not to laboratory conditions\textsuperscript{10,11}. While not truly equilibrium configurations relative to laboratory conditions, the as-mined configurations \textit{appear} to be such because the kinetics of relaxation are immeasurably slow unless the structures undergo significant perturbations. We caused these perturbations by heating or solvent exposure of the samples. In the case of the present decompression experiments, the relaxation of some high pressure-induced configurations can perhaps occur at a measurable rate only if the driving force is high enough, as a result of a much lowered pressure around the sample.

It was thus hypothesized that the hysteresis loop obtained at high pressures may well be attributable to a kinetic effect, reflecting the speed with which the coal network relaxed during decompression. Several experiments were performed to test this hypothesis. In one series, decompression of a freshly compressed sample (227 MPa) was permitted to occur down to various pressures between 20 and 227 MPa, followed immediately by recompression. The result was always a very close retrace of the \textit{decompression} curve between these pressures. This demonstrated that there is a reversible component of compression (uptake does continually decrease with decrease in pressure) that acts independently of some more difficult-to-reverse component.
On the other hand, decompressing the samples to ambient always closed the hysteresis loop, after the first compression/decompression cycle (see Figures 4 and 5). The kinetics of restoring the coal structure to near its new atmospheric pressure equilibrium state can be quite fast near ambient pressure, i.e. no delay was needed before starting the next cycle in the case of Pittsburgh No. 8 coal, and a few hours of ambient pressure exposure are needed for Illinois No. 6 coal.

Further information as to the nature of the hysteresis came from another type of experiment. These tests involved permitting a sample to stand at 34.5 or 68.9 MPa for two hours while continuously recording the "uptake" or "extrusion" volume. The results indicated that at these intermediate pressures, there is apparently no measurable rate of mercury extrusion; "uptake" values did not significantly change during the period of holding a constant pressure. There however appeared to be some effect of holding time on compression values at high pressure. The longer that a sample was held at a particular pressure, the higher the "uptake" value obtained, closing about a quarter of the gap between the decompression and compression curves. Thus it appears that the magnitude of the compression value is determined by two factors - the pure, bulk compressibility and the kinetics of some kind of slow structural reorganization.

A similar hysteresis behavior was observed by another worker using very different experimental techniques. Brenner\textsuperscript{12} has performed compressive testing of pyridine-swollen thin sections of coal. His tests were classical stress-strain measurements in which the load is applied in one coordinate direction, as distinct from the measurements of compressibility performed here. The unidirectional stress experiment provides the "tangent Young's modulus" or "dynamic Young's modulus," \(E (\equiv \text{tensile stress} / \text{tensile strain})\). The relationship between \(E\) and \(B\) is through the Poisson ratio (\(v\)) of the material, defined as the (change in width per unit width / change in length per unit length) in tensile-type experiments. The moduli are related by:

\[
E = 3B (1 - 2v)
\]

For organic liquids, the Poisson ratio is exactly 1/2 in value, and the relationship between the moduli is trivial, in that liquids cannot support a tensile stress. For polymers, \(v\) can be significantly less than 1/2. For example, polyethylene has \(v = 0.49\), PMMA has \(v = 0.4\) and polystyrene has \(v = 0.38\). The Poisson ratio for coals was estimated in one study to be fairly constant at 0.35, at least up to very high ranks of coal\textsuperscript{13}. There was, however, some variability in values reported for
coals by other workers; values were found to be in the range 0.37 to 0.44\textsuperscript{14}. If the lower range of values for Poisson's ratio is correct, then value of E should be numerically quite close to the value of the bulk modulus B, and in any case E will always be of the same order of magnitude as B.

The measurements of Brenner\textsuperscript{12} showed that the stress-strain curves of swollen coals are characterized by hysteresis, relative to compression and decompression. The slope of the compression cycle was always gentler than the slope of the decompression cycle at high stresses. This naturally means that E is greater during the decompression than during the compression cycle, at high load. At low loads, the opposite appears to be true. Our results for B follow exactly the same trend. At high loads (high pressures) the volume change with change in pressure is greater during compression than decompression, which means that B is higher for decompression than compression, at high loads. The hysteresis in the stress-strain curves is thus observed in two very different tests.

Brenner also noted that the recovery of the coal to its initial unstressed volume can be slow or impossible even at zero stress. On repeated cycles, the recovery to the new volume can be fast at zero stress. This echoes our finding that there is a definite kinetic limitation in recovery of the material, and our results go further to suggest that recovery is essentially impossible, except for near zero stress. It is notable, however, that Brenner performed his measurements on rubbery coals and obtained characteristics somewhat similar to what we observe with coals presumed to be in the glassy state.

The above observations raise the question as to whether our compression or decompression value of B is "correct". Similar questions come up often in mechanical testing of polymeric materials, in which the time history of testing is important. The behavior we observe is characteristic of a macromolecular network with high internal viscosity. This normally forces distinguishing between dynamically and statically determined mechanical properties, and the "correct" value depends entirely upon the intended use of the data. In the case of coals, there is the question of whether to use the compression or decompression value of B to "correct" classical porosimetry results. Use of the initial compression may be justified. The slow relaxation upon decompression gives a lower apparent high-pressure compressibility, but the compression upon initial intrusion would, however, not be subject to the same kinetic limitations, as noted above.
Table 2 gives values for both compression and decompression values of compressibility that we obtained from the highest pressure linear portions of the respective curves. The tabulated values are \( (1/B\rho = \kappa/\rho) \), where \( \rho \) is the initial coal density. The results for Illinois No. 6 and Pittsburgh No. 8 show the extent to which the results are reproducible. It appears that values of \( (\kappa/\rho) \) have uncertainties of about 10% around a mean. For comparison, if a coal density of 1.3 g/cc is assumed, then our apparent values of \( B \) from the compression cycles range from 2.6 to 8.5 GPa, which are in good agreement with the values obtained by others of 4.3 to 13 GPa\(^2\), 4.6 to 9.0 GPa\(^3\), and 7.7 GPa\(^4\).

The results for the Pittsburgh No. 8 coal show that an extracted coal has a slightly higher compressibility than a raw coal. This may result from two contributions. Removal of extractable material from a matrix might be expected to create more internal voidage and, therefore, compressibility. In addition, the structure of the coal is relaxed by pyridine swelling\(^1\). There is not a very strong variation of compressibility with rank, as is apparent from a comparison of the results of the bituminous coals and the lignites. There is at most a factor of three spread in all compressibility values.

The shear modulus of a material \( (G) \) is defined by (shear stress / shear strain) and is related to the other previously quantities as well:

\[
E = 2G \left(1 + \nu\right) = 3B \left(1 - 2\nu\right)
\]

(3)

As has been shown by Larsen and Kovac\(^16\), application of measured or estimated values of \( G \) or \( E \) for coals to rubber elasticity models gave seemingly unrealistic values of molecular weight between crosslinks. In their study \( E \) was typically of order \( 10^9 \) Pa, and thus from equation (3) and the values of \( \nu \) reported above, \( G \) was of the same order of magnitude. In fact, by use of (3), and by
using an approximate value of density, \( \rho = 1.3 \text{ g/cm}^3 \), it can be clearly seen that the results of Table 2 also will yield estimates of \( E \) or \( G \) which are of the same order of magnitude.

Thus there is great consistency among all of the data that have been produced on the mechanical properties of coals, and all imply very high values of the moduli. Such high moduli in polymer systems are generally associated with the glassy state\(^7\). Even in the presence of water, a known plasticizing agent for transport in coals\(^7\), the coals are seen to be glassy, rather than rubbery. This is of little surprise, considering that the fracture behavior of wet lignites is still much more glassy than it is rubbery.

Coal is in a rubbery-like state only in the presence of good swelling solvents. This is clearly seen in the experiments by Brenner, which gave moduli of order \( 10^6 \) Pa for pyridine immersed samples\(^12\). Such moduli are very typical for polymeric systems in which crystallinity is not high, and can be observed over a wide range of temperatures if the polymer is crosslinked\(^7\). A coal's structure may be relaxed by solvent preswelling or by the action of heat, but that does not mean that its structure will be made permanently rubbery. From our results, it is clear that coal remains quite glassy at room temperature, even after pyridine extraction. The structure will be rubbery only in the presence of a good solvent. Also, the mere presence of a swelling solvent in the structure, e.g. water in lignites, does not assure the attainment of a rubbery state.

Considering the glassy nature of the coal in the compression tests that we have performed, it then comes as little surprise that there is a marked degree of hysteresis observed in the compression-decompression cycles. The relaxation of a glassy structure would be expected to be observable only over a very long timescale, if the driving force for relaxation is small. Again, the creep behavior of coals is known to be characterized by long timescales\(^18,19\). It appears that only when the structure is far out of equilibrium with respect to prevailing conditions, will it be driven towards a new configuration on the timescale of the experiments performed here.

**CONCLUSIONS**

It has been noted that there is no single, distinct measure of the bulk modulus of coals measurable in mercury porosimetry experiments. As with other modulus measurements on coal, there is a hysteresis associated with these measurements of bulk modulus. The hysteresis is
presumably associated with the time-dependent reorganization of its macromolecular network structure, in response to the applied stresses.

The above results confirm what has been inferred from other types of measurements on the porosity and surface areas of coals. It has been concluded that because coal behaves as a viscoelastic gel (as opposed to a rigid solid) on the timescales of interest, then many of the “classical” characterizations of porosity might provide a misleading picture of the structure of coals. Here, it has been specifically concluded that “corrections” for coal compressibility, commonly used in mercury porosimetry work on raw coals, are subject to some uncertainty from this source. At the higher temperatures of actual coal processing, and especially in the presence of solvents, there is an even greater uncertainty concerning the applicability of these measurements, since the physical structure of the coal can be dramatically altered.6,7,10,11

The apparent bulk moduli of coals do not vary widely with rank. The pre-extraction of the coal or presence of water in the coal affect the moduli by only a small amount. Water is an effective swelling agent for low rank coals, swelling lignites by 30 to 40%, relative to a dry state.7 There is, however, no evidence from the values of bulk modulus obtained here that the rubbery state of the coal, as is attainable in pyridine swelling of higher ranks, exists in the wet lignites. We therefore indirectly support earlier workers20 in their conclusion that the effect of moisture content on dynamic moduli is small.

REFERENCES


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</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</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</td>
<td>60.9</td>
<td>4.2</td>
<td>0.6</td>
<td>1.4</td>
<td>8.2</td>
<td>24.7</td>
<td>30.7</td>
<td>28.9</td>
</tr>
<tr>
<td>Pittsburgh No. 8 HVBit.(^a)</td>
<td>75.5</td>
<td>4.8</td>
<td>1.5</td>
<td>2.2</td>
<td>9.3</td>
<td>6.7</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Illinois No. 6 HVBit.(^a)</td>
<td>65.7</td>
<td>4.2</td>
<td>1.2</td>
<td>4.8</td>
<td>15.5</td>
<td>8.6</td>
<td>8.0</td>
<td>10.3</td>
</tr>
<tr>
<td>Powhatan No. 5 HVBit.</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.

\(^a\)- Argonne National Laboratory Premium Coal Samples\(^8\).
<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Pretreatment</th>
<th>Compressibility, ( k/p ) (cc/g-Pa ( \times 10^{10} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Compression</td>
</tr>
<tr>
<td>Beulah lignite</td>
<td>As-received</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Dried(^a)</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>(Mean)</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Heated(^b)</td>
<td>2.2</td>
</tr>
<tr>
<td>Freedom lignite</td>
<td>As-received</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Dried(^a)</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Dried(^c)</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Heated(^d)</td>
<td>1.7</td>
</tr>
<tr>
<td>Glenn Harold lignite</td>
<td>As-received</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>Dried(^a)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Dried(^c)</td>
<td>1.8</td>
</tr>
<tr>
<td>Gascoyne lignite</td>
<td>As-received</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>Dried(^a)</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>(Mean)</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Dried(^e)</td>
<td>1.2</td>
</tr>
<tr>
<td>Pittsburgh No. 8 HVB(^i)</td>
<td>As-received</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>(Mean)</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>Pyridine Extracted</td>
<td>1.8</td>
</tr>
<tr>
<td>Illinois No. 6 HVB(^i)</td>
<td>As-received</td>
<td>2.54</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>2.95</td>
</tr>
<tr>
<td></td>
<td>(Mean)</td>
<td>2.89</td>
</tr>
<tr>
<td></td>
<td>&quot;</td>
<td>2.79</td>
</tr>
<tr>
<td>Powhatan No. 5 HVB(^i)</td>
<td>As-received</td>
<td>1.2</td>
</tr>
</tbody>
</table>

a. Room temperature dried for 30 days at 0% relative humidity.
b. Heated at 573 K for 30 minutes.
c. As in a., plus 30 minutes at 373 K.
d. Heated at 573 K for 24 hours.
e. Dried at 373 K for one hour.
Mercury uptake is relative to a zero uptake reference point at an applied mercury pressure of 0.4 MPa. The sample marked 100% RH, 298 K refers to a sample equilibrated over pure water at 298 K for 30 days; the sample was not dried prior to analysis, but there was a possibility of moisture loss, relative to the as-mined condition, due to the difficulty of maintaining true 100% relative humidity in a chamber which had to be periodically opened. The sample marked 0% RH, 298 K was dried at room temperature for 30 days over concentrated sulfuric acid. The sample marked 0% RH, 298 K+0% RH, 373 K involved room temperature drying as described above, followed by one hour at 373 K. Arrows on the curves indicate whether the experiment involved compression or decompression.
Figure 2. The results of a single compression-decompression cycle performed on Pittsburgh No. 8 high volatile bituminous coal. The sample was used as-received.
Figure 3. The results of a single compression-decompression cycle performed on Powhatan No. 5 high volatile bituminous coal. The sample was used as-received.
Figure 4. The results of multiple compression-decompression cycles performed on Illinois No. 6 high volatile bituminous coal. The sample was used as-received (undried). The arrows indicate whether the experiment involved compression or decompression. All decompressions followed the same path. Long dashes - first compression; short dashes, second compression; dotted curve, third compression.
Figure 5. The results of multiple compression-decompression cycles performed on Pittsburgh No. 8 high volatile bituminous coal. The sample was pyridine extracted and dried at 373 K prior to analysis. The arrows indicate whether the experiment involved compression or decompression. All decompressions followed the same path. Long dashes- first compression; short dashes, second compression; dotted curve, third compression.
END

FILMED

DATE

1/29/94