수은 공극률측정법을 이용한 석탄의 탄성특성 연구

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Elastic Behavior of Coals Studied by Mercury Porosimetry

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INTRODUCTION

Mercury porosimetry has been widely used to examine the pore structure of solids. The method has found frequent application in examination of coals. Questions have recently been raised about the value and 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 tramsport rates 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 described 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 high 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. Recent work has suggested that the correction of porosimetry results for sample compression might not be a straightforward as earlier believed, and it is suggested that it might be more difficult to seperate pore filling from compression than earlier believed.

Since coal is a macromolecular solid, it exhibits certain characteristics seen also in polymers. Among these is viscoelastic response to applied stresses. It is this aspect of coal's structure that is probably involved in certain aspects of coal's behavior during porosimetry, as will be outlined below.

EXPERIMENTAL

Coal samples were -20+100 mesh in size. Mercury porosimetry was carried out using a standard Quantachrome Instruments mercury porosimeter. This instrument can be used to scan mercury pressures up tp 227 MPa (33,000 psia). Normally the instrument scans at 45.5 MPa/min. In a departure from common practice, here both compression and decompression cycles were examined.

RESULTS AND DISCUSSION

Figure 1 shows a typical result from mercury porosimetry. In this study the main focus is on the high pressure, fairly rectilinear portions of the compression curves, and the hysteresis observed in this region. There is always a hysteresis evident in the compression-decompresison cycles for all samples tested. It is this hysteresis behavior that is an indication of the macromolecular behavior of coal. In the case of the Glenn Harold lignite (Figure. 1), the nearly linear part of the compression curve is seen to begin at almost 50 MPa. The compressibility that has normally been used for correcting porosimetry results is that from the high pressure compression part of the porosimetry experiment; generally, not very much attention has been paid to the decompression part of the cycle.

Sample preparation was seen to influence the results obtained during porosimetry. Figure 1 shows the effect of drying a sample. The dried lignite samples (whether dried at room temperature or at 373 K) show a higher uptake of mercury than the wet sample. This is most readily visible from the mercury uptake at low pressures, under which conditions there would be little argument about the interpretation in terms of pore filling. This might not be considered surprising, in that water has been removed from the lignite. It is important, however, to recognize that upon drying, the lignite gel structure collapses, thus there is not nearly as much porosity created as the amount of water removed (30-40% by mass of most lignites) might suggest. Significant amounts of mesoporosity and macroporosity do, however, survive and are created by the drying.

The dried and undried materials of Figure 1 are also very different in macromolecular structure, in that the dried lignite has a much more compact network structure than the wet lignite. Considering the major difference in structure, there is surprisingly little difference to be seen in the high pressure compression behavior. There is a question as to whether the water that was originally associated with the coal is retained during compression. The similarity of the high pressure results might not be surprising if the water partitions into the mercury phase at high pressures.

To explore the observed hysteresis behavior more fully, 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 2. Such behavior has also been observed in very different kinds of materials (e.g., alumina-silica gel). Also, after the first compression-decompression cycle, all subsequent compression curves were essentially identical, implying that the changes in the sample had become fully reversible, even though always characterized by hysteresis. This clearly shows that the hysteresis is not simply a consequence of an irreversible alteration of the coal's structure, since this would not be a reversible, and would not give rise to reproducible curves, cycle to cycle. This is not to say that permanent physical changes cannot be induced by compression.

As a thermodynamic property, the bulk compressibility would not be expected to be path-dependent. If the high pressure behavior was determined purely by sample compression, then the extent to which the sample is compressed (resulting in some value of apparent mercury uptake) should not depend upon what happened earlier to the sample. Thus the observed hysteresis displayed in Figures 1 and 2 must be viewed as inconsistent with simple interpretations of the high pressure behavior in terms of pure compressibility.

Table 1 gives values of the apparent compressibility that are obtained from the linear portions of the compression and decompression curves. The tabulated values are ($1/B\rho = \kappa/\rho$), where ρ is the initial coal density. It is observed in all cases that the apparent compression values are higher than the decompression values, reflecting the exsitence of hysteresis in all cases.

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

$E = 2G(1+\nu) = 3B(1-2\nu)$, where ν is the Poisson ratio of the material, defined as the (change in width per

width/change in length per unit length) whereas E is Young's modulus and B is bulk modulus.

By use of the above equation and by assuming an approximate value of density for coal as 1.3, the results in Table 1 yield estimates of E or G as an order of 10^9 Pa which is consistent with earlier reported values. There is great consistency among all of the data that have been produced on the mechanical properties of dry and as-received coals, and all imply very high values of the moduli. Such high moduli in ordinary polymer systems are generally associated with the glassy state. The values of E for low and medium rank coals are comparable to those for phenol-formaldehyde resins, which are often used as models of coal structure.

CONCLUSIONS

The apparent bulk moduli of coals do not vary widely with rank, but there is variation coal-to-coal. The pre-extraction of the coal tends to increase the apparent compressibility, as does heat treatment. These results support that the effects of moisture content on dynamic moduli is small and also are consistent with the fact that dry coal is a glassy solid. The data presented here and elsewhere suggest that the coal exhibits delayed elasticity and that this is related to a significant degree of difficulty in reordering the macromolecular network structure upon stressing.

Because coal behaves as a viscoelastic gel (as opposed to a rigid solid), many of the classical characterization of porosity might provide a misleading picture of the accessibility of coals. At the temperatures of actual coal processing, especially in the presence of solvents, there is an uncertainty concerning the applicability of the ordinary porosimetric and surface area measurements, since the physical structure of the coal can be dramatically altered. The present procedure, involving use of the compressibility derived from the first compression cycle appears reasonable, since this is the compressibility at the time of the actual pore intrusion.

Table 1. Summary of Compressibility Measurements

SAMPLE	Pretreatment	Compressibility, κ/ρ (cc/g-Pa x 10^{10})	
		Compression	Decompression
Beulah-Zap lignite	As-received	1.7	0.35
	Dried[a]	1.7 (±0.3)	0.95 (±0.26)
	Heated[b]	2.2	0.90
Freedom lignite	As-received	1.4	0.97
	Dried[a]	1.4	1.4
	Dried[c]	1.4	0.83
	Heated[d]	1.7	1.0
Glenn Harold lignite	As-received	1.8	0.83
	Dried[a]	1.1	0.61
	Dried[c]	1.8	1.0
Gascoyne lignite	As-received	1.5	0.69
	Dried[a]	1.4 (±0.05)	0.60 (±0.18)
	Dried[e]	1.2	0.69
Pittsburgh No.8 HVB	As-received	1.1 (±0.2)	0.61 (±0.03)
	Pyridine Extracted	1.8	0.98
Illinois No.6 HVB	As-received	2.79 (±0.25)	0.90 (±0.09)
Powhatan No.5 HVB	As-received	1.2	0.76

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; HVB: high volatile bituminous

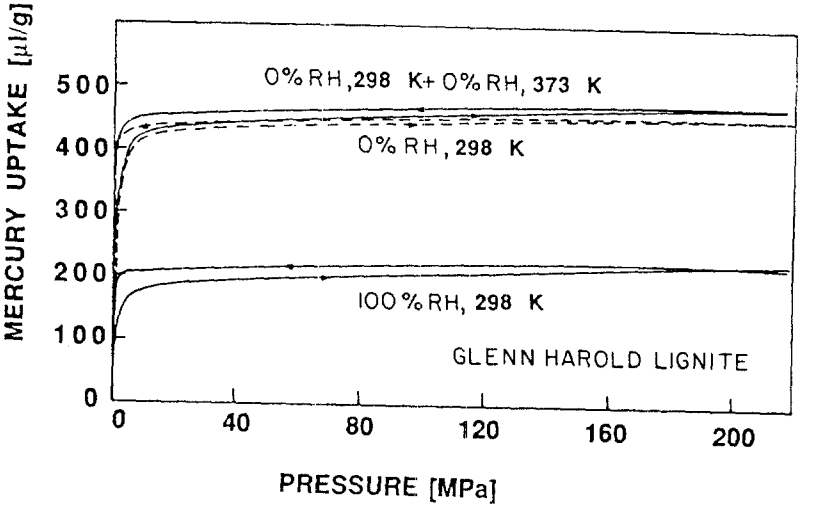

Figure 1. Results of first compression-decompression cycles on Glenn Harold North Dakota lignite.

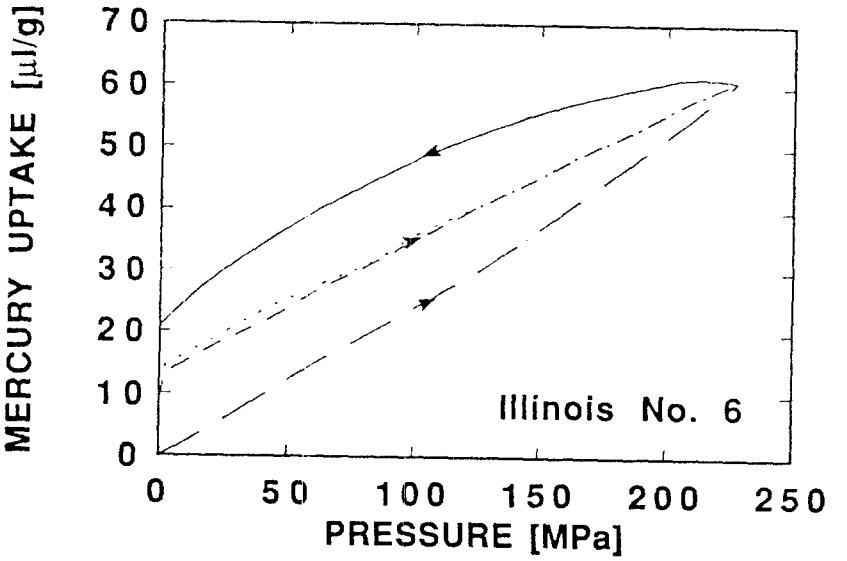

Figure 2. The results of multiple compression-decompression cycles performed on Illinois No.6 high volatile bituminous coal; Long dashes, 1st compression; short dashes, 2nd compression; dotted curve, 3rd compression.