

# Transport of Penetrants in the Macromolecular Structure of Coals. V. Anomalous Transport in Pretreated Coal Particles

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## Synopsis

Dynamic swelling studies were performed on well-characterized coal particles treated in various ways. Pyridine was the penetrant and all studies were performed at 35°C. The transport behavior was compared for untreated, pyridine-extracted, oxidized and alkylated samples. Data analysis using an exponential equation of the penetrant uptake as a function of time and a relaxation-controlled analysis showed that the pyridine transport mechanism was non-Fickian or Case-II transport, and that it was only slightly affected by the pretreatment of the coal samples.

## INTRODUCTION

In recent years, significant research has been done on the analysis of the molecular structure of the organic phase of bituminous coals. Mainly through the work of Larsen, Peppas and their collaborators,<sup>1-8</sup> we are able to present now a generalized view of the coal structure as a high cross-linked macromolecular network. It is interesting that this idea has been proposed by van Krevelen<sup>9</sup> more than twenty years ago, but it was only in recent years that this structure was proven through theoretical analysis,<sup>1,10</sup> swelling experiments,<sup>2,3,6,7,11</sup> and mechanical tests.<sup>8,12</sup>

As discussed before,<sup>6</sup> the network structure of coal consists of highly aromatic and heterocyclic structures joined together by junctions which may be covalent bonds, hydrogen bonds, or simply permanent physical entanglements. This structure is highly cross-linked. Thus, its analysis required the development of novel swelling and deformation theories<sup>11</sup> based on non-Gaussian distribution of its constituent chains.

The use of dynamic swelling experiments as a method to probe the macromolecular structure has been suggested by various investigators,<sup>13-19</sup> although it is not clear that meaningful structural results can be obtained. This happens because the coal cross-linked structure may be affected by thermodynamically good penetrants, which tend to show specific thermodynamic interactions (i.e., non-random mixing). For example, it has been proposed that penetrants such as pyridine may destroy some of the hydrogen bonds responsible for the highly cross-linked coal structure.<sup>11,20</sup>

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In any case, dynamic penetrant transport analysis of coal networks is important because it allows a better understanding of the mechanisms of transport of coal "solvents" at various temperatures. Since coal is believed to be similar in nature to a glassy polymeric network, with glass transition temperatures ranging from 300 to 350°C, penetrant transport in coal particles presents the interesting characteristics of Fickian or non-Fickian diffusion.

In the previous contributions in this series,<sup>21-24</sup> we investigated the mechanisms of pyridine transport in coal particles and the effect of particle size and porous structure on the dynamic swelling of the coal proper. We offered a mathematical analysis of the overall transport phenomenon and we examined the similarities and differences between transport in coal networks and certain highly crosslinked, rigid polymeric structures. In fact, we proved<sup>23</sup> that poly(1,4-dimethylnaphthaleno-2,5-dihydroxybenzene), a polymer synthesized by Squires et al.,<sup>25</sup> simulates rather remarkably the coal structure.

Analysis of the penetrant sorption data in coal particles can be accomplished by various means. For example, a convenient method of analysis involves fitting of the sorption data to the empirical equation,

$$\frac{M_t}{M_\infty} = kt^n \quad (1)$$

Here,  $M_t$  is the mass of solvent imbibed at time  $t$ ,  $M_\infty$  is the mass of solvent imbibed at long times, and  $k$  is a constant which depends on the structural characteristics of the material and on the solvent/material interactions. The exponent  $n$ , is used to indicate the type of diffusion and to infer state changes in the macromolecular system. For microspheres,<sup>24</sup> when  $n$  is equal to 0.43, the diffusion is Fickian; when  $n$  is 0.85, Case II transport occurs; finally, values of  $n$  between 0.43 and 0.85 indicate anomalous transport. If  $n > 0.85$ , the swelling material is likely to craze and fracture due to the osmotic pressure differences at the accelerating and advancing front. This type of transport mechanism is known as Super Case II transport. Equation (1) is useful for preliminary analysis of sorption data, although it may only be used up to 60% of the final weight of solvent imbibed and it has no provisions for analysis of details, such as inflections or solvent loss with time.<sup>26</sup> Thus, there is no phenomenological connection of the model with the data.

Experimental results from sorption studies on polymers and other glassy macromolecular structures show that in the majority of cases, the observed transport mechanism was neither Fickian nor Case II transport, but anomalous transport. Equations (2) and (3) are the Fickian and relaxation-controlled equations for transport into a sphere, respectively.

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-Dn^2\pi^2 \frac{t}{a^2}\right) \quad (2)$$

Here  $M_t$  is the weight of solvent gained at time,  $t$ ,  $M_\infty$  is the solvent gained at long times,  $D$  is the concentration-independent diffusion coefficient, and  $a$  is

the radius of the sphere. The equation for relaxation-controlled transport<sup>27</sup> is

$$\frac{M_t}{M_\infty} = 1 - \left(1 - \frac{k_0 t}{C_0 a}\right)^3 \quad (3)$$

where  $k_0$  is the Case II relaxation constant (g/cm<sup>2</sup> min) and  $C_0$  is the equilibrium concentration of penetrant (g penetrant/cm<sup>3</sup> polymer). Analysis of sorption data with the semiempirical diffusion Eq. (1) and these two equations can lead to the determination of the controlling transport mechanism, and therefore, to the determination of the state of the polymer and the effectiveness of a specific penetrant.

Various parameters are critical in the interpretation and modeling of sorption data including temperature, particle size and shape, sample history and activity of the penetrant.

Sample pretreatments affect both the rate of sorption and the equilibrium sorption.<sup>29</sup> It was found that preswelling accelerates the sorption rate and increases the apparent equilibrium concentration, while preannealing (drying under vacuum at higher temperatures) has the opposite effect. However, Berens and Hopfenberg<sup>27</sup> observed that at very long times, the equilibrium concentrations for preswelled and preannealed samples approached the same value. They speculated that initial sorption is Fickian, where the penetrant molecules move into the existing free-volume of the polymer. Subsequent time-dependent polymer relaxations in the form of group rotations opened up more free volume sites, allowing the penetration of more sorbate. If this is so, then a sample which has been pre-exposed to the penetrant will have already experienced initial hole filling and either have completed or be in the process of segmental relaxations. Obviously careful experimentation and critical scrutiny of the resulting data is mandatory even for well-characterized polymer/penetrant systems.

In the present work we report for the first time important new data on the pyridine transport through pretreated coal network structures, with emphasis on the transport mechanisms.

## EXPERIMENTAL

### Sample Preparation

Coal samples ground to an average particle size of 20–30 mesh (600–850  $\mu\text{m}$ ) and packed under nitrogen into stainless steel cans, were furnished by the coal bank group of Pennsylvania State University (PSU). The identification numbers used throughout the chapters on experimental procedures, results, discussion and conclusions are those assigned by PSU and are shown in Table I.

The coal samples were sieved to 20–30 (600–850  $\mu\text{m}$ ) and 80–100 mesh (150–180  $\mu\text{m}$ ) with ASTM approved stainless steel sieves at room temperature under nitrogen for one minute or less to avoid formation of fines.

Extraction separates the coal matrix from material which is free or loosely held in the interstices. In a typical extraction, a coal sample of 20–30 mesh particle size and approximately 3.0 g was weighed to  $\pm 0.0001$  g, placed in a

TABLE I  
Analysis of PSU Coal Samples Used in this Study

PSOC code #	County, state	Rank	% C (dmmf)	% O (dmmf)	%mm (dry)
418	Titus, TX	LigA	69.94	21.46	27.50
791	Titus, TX	LigA	72.25	20.17	20.77
247	Burke, ND	LigA	75.53	17.61	12.77
312	Navajo, AR	HVC	78.38	14.16	7.08
207	Lawrence, OH	HVB	79.82	12.23	9.10
853	Delta, CO	HVC	80.12	12.68	3.74
402	Craig, OK	HVA	82.48	9.00	18.54
989	Greenbrier, WV	MVB	88.19	3.76	5.08

Abbreviations: LigA = lignite, HVC = high volatile C bituminous, HVB = high volatile B bituminous, HVA = high volatile A bituminous, MVB = medium volatile bituminous.

cellulose Whatman extraction thimble of medium porosity, and the thimble placed in a Soxhlet extraction apparatus. All extractions were carried out under nitrogen using pyridine at its atmospheric boiling point of 115.5°C. Recycling typically occurred about four times an hour. The extract solution was replaced every one to four days with fresh pyridine extraction periods of one to eight weeks. Acetone was then used as the extraction solvent at its atmospheric boiling point of 56.2°C for 24 h to sweep out pyridine. At the completion of this process, the extracted residue was dried to constant weight under vacuum at ca. 60°C and ca. 0.93 MPa (700 torr) under flowing nitrogen. The residue was weighed and stored under nitrogen.

### Atmospheric Oxidation

Atmospheric oxidation was performed to investigate its effects on the cross-linked macromolecular structure of coal and dynamics of the sorption of pyridine. The 20–30 mesh coal sample was maintained at a temperature range of 61 to 63°C with air flowing over it for one week.

### Liotta Oxygen Methylation

Coal owes some of its cross-linked nature to the presence of hydrogen bonds between phenolic and carboxylic groups. A complete characterization of the macromolecular structure of coal obviously includes the percentage of cross-linking arising from hydrogen bonds. The Liotta *O*-methylation<sup>30</sup> was developed specifically to first swell the coal sample, thereby opening up reaction sites, and then to neutralize the phenolic and carboxylic functionalities by replacing their hydrogens with a methyl group.

A 5 g sample of coal particles of 80–100 μm was suspended in tetrahydrofuran (THF) in a 500 ML three-neck round-bottom flask at room temperature under nitrogen. Ten cm<sup>3</sup> of a 40 wt% aqueous solution of tetrabutylammonium hydroxide (TBAH) were added, under agitation, to the suspension until a neutral pH was reached. This served to remove all acidic protons in the coal. Another 0.2 gEq of TBAH were added and the mixture was stirred for two hours. Iodomethane as the alkylating agent was added in twofold excess, or

approximately 3 cm<sup>3</sup>, and stirring was continued overnight. The volatile materials were removed by a mild vacuum distillation in the rotating evaporator at 50 to 70°C. Then, the TBAH was removed by washing with water several times. The methylated coal was then dried under vacuum of ca. 667 Pa (5 torr) at 120°C for 24 hours to constant weight. Infrared spectroscopy (IR) of the methylated coal in KBr pellets was used to verify the methylation of the samples.

### Dynamic Swelling Studies

Dynamic swelling studies were performed using pyridine at 35°C. The technique was basically that described before by Peppas and Lucht.<sup>21</sup> The samples were weighed as a function of time.

## RESULTS AND DISCUSSION

Several effects were investigated by pyridine sorption on the various coals studied. Here we present the results of the coal PSOC-207, as an example. Of this coal, there were prepared in five samples (i) 20–30 mesh (600 to 800 μm), untreated particles; (ii) 80–100 mesh (150 to 180 μm), untreated particles; (iii) 20–30 mesh particles which had been pyridine extracted as described; (iv) 20–30 mesh particles which had been oxidized with air at 60°C for seven days; and (v) 60–100 mesh (150 to 250 μm) particles which had been oxygen methylated by the technique of Liotta<sup>30</sup> to remove the potential for hydrogen bonding. The samples were vacuum-dried at 3400 Pa (25 torr) and 60 ± 3°C for 24 hs. Sorption was performed at 3.50 ± 0.5°C for 770 hs in a dessicator. Table II gives the values of sorption at equilibrium of the various samples tested. Figures 1 through 4 show the sorption data as a function of the square root of time.

Figure 1 compares the sorption values of the two samples of particle sizes 20–30 and 80–100 mesh. The sorption uptake isotherm for the sample of 20–30 mesh particles has a more pronounced S-shaped curve than does the

TABLE II  
Values of Pyridine Equilibrium Uptake,  $M_t/M_\infty$  [g penetrant/g coal (mmf)]

Condition of sample	Particle size	$M_t/M_\infty$
Untreated	20–30 mesh (600–850 μm)	0.622
Pyridine extracted	20–30 mesh (800–850 μm)	0.574
Oxygen methylated <sup>2</sup>	60–100 mesh (150–250 μm)	—
Untreated	80–100 mesh (150–180 μm)	0.636
Air-oxidized	20–30 mesh (600–850 μm)	0.610

<sup>a</sup>Samples of PSOC-207, 79.82°C (dmf) pyridine vapor swelled at 35°C and atmospheric pressure for 770 hs.

<sup>b</sup>Equilibrium not reached due to slow volatilization of sample during swelling.

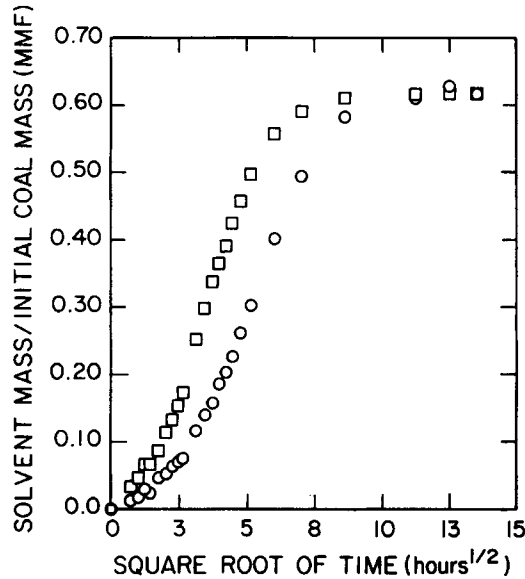


Fig. 1. Dynamic swelling of untreated coal particles of PSOC-207 with 79.82% C (dmmf) by pyridine vapor at 35°C. Mesh size: (○) 20–30, (□) 80–100.

isotherm for the sample of 80–100 mesh particles. The sample of 80–100 mesh particles sorbed more rapidly than the sample of 20–30 mesh particles in the initial sorption process. However, after 100 hs of exposure to pyridine the values of the solvent uptake in the two samples were approximately equal, at  $M_t/M_i = 0.64$  g solvent/g coal for the 80–100 mesh sample and at  $M_t/M_i = 0.62$  g solvent/g coal for the 20–30 mesh sample.

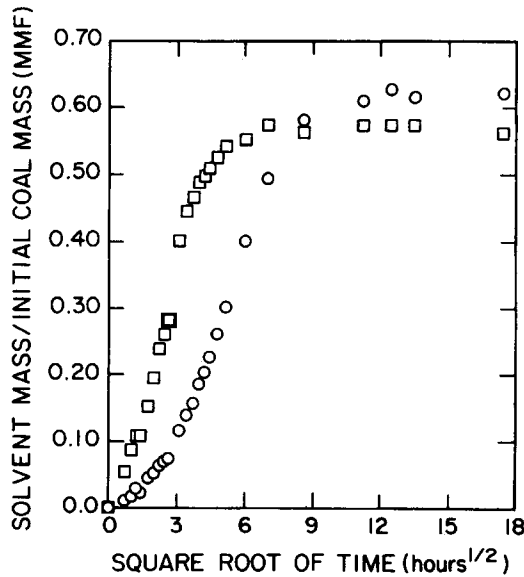


Fig. 2. Dynamic swelling of 20–30 mesh coal particles of PSOC-207 with 79.82% C (dmmf) by pyridine vapor of 20–30 mesh coal particles at 35°C. Sample condition: (○) untreated, (□) pyridine-extracted.

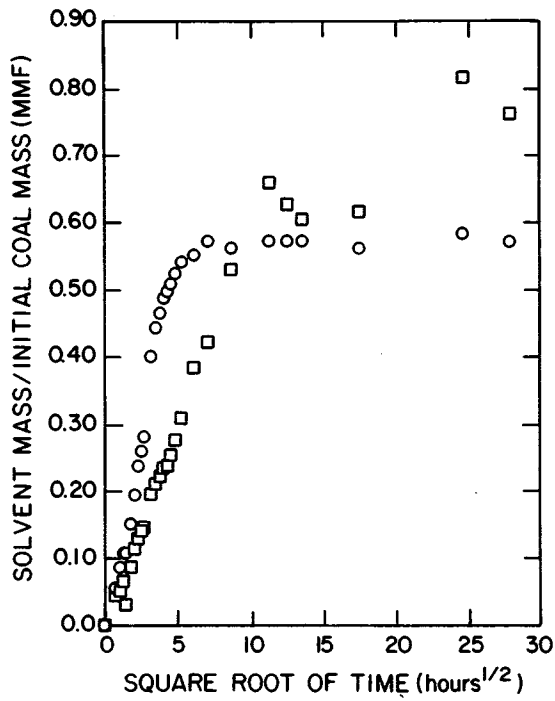


Fig. 3. Dynamic swelling of PSOC-207 particles with 79.82% C (dmmf) by pyridine vapor at 35°C. Sample condition: (○) 20-30 mesh, pyridine-extracted, (□) 600-100 mesh, oxygen-methylated.

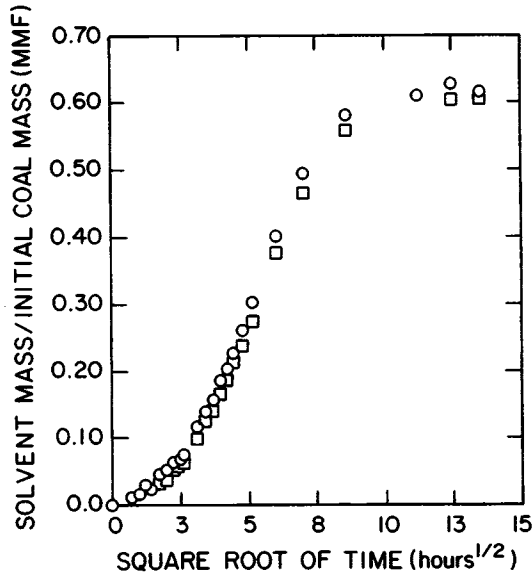


Fig. 4. Dynamic swelling of 20-30 mesh coal particles of PSOC-207 with 79.82% C (dmmf) by pyridine vapor at 35°C. Sample condition: (○) untreated, (□) air-oxidized.

The sorption data for the samples of untreated and pyridine-extracted PSOC-207 are shown in Figure 2. The extracted sample of PSOC-207 sorbed pyridine more rapidly than the untreated sample and reached swelling equilibrium after approximately 80 hs, while swelling equilibrium in the untreated sample was not achieved until a sorption time of about 400 hs. The sorption isotherm for the pyridine-extracted sample of PSOC-207 is not S-shaped. The swelling data for the sample of untreated PSOC-207 had a pronounced S-shaped isotherm and reached the same equilibrium sorption value,  $M_t/M_i = 0.62$  g solvent/g coal, as the pyridine-extracted coal. The rapid sorption uptake by the pyridine-extracted coal was of course due to its preexposure to pyridine.

Figure 3 compares the dynamic swelling data for the sample of 20–30 mesh, pyridine-extracted particles with the sorption data for the sample of 60–100 mesh, *O*-methylated particles. The initial rate of sorption was more rapid in the pyridine-extracted samples, but a swelling equilibrium where the solvent uptake equaled  $M_t/M_i = 0.62$  g solvent/g coal was reached by 80 hs, while the *O*-methylated samples continued to sorb pyridine and exhibited at least two regions of solvent weight loss. Swelling equilibrium was not achieved in the *O*-methylated sample as some portion of the sample was volatilized and lost during the sorption time of 770 hs. This volatilization process was an indication of severe degradation of the coal network.

Figure 4 shows the swelling results for samples of 20–30 mesh particles, one of which was oxidized with air and the other untreated. The solvent uptake isotherms were indistinguishable. Chemical analysis showed that coal sample PSOC-207 was already air-oxidized as its sulfate content was far greater than 0.5%.

The values of the exponent  $n$  for all data sets and of the statistical parameters of the fit are shown in Table III. The relaxation constant,  $k_0$ , the equilibrium concentration of penetrant,  $C_0$ , and the statistical parameters from the fit of Eq. (3) are shown in Table IV. Only the data indicating Case-II or close to Case-II transport were analyzed in the latter case.

From these results we conclude that the transport mechanism remains anomalous (non-Fickian) after Liotta *O*-methylation of coal sample PSOC-207. However, the values of the exponent, with 95% confidence limits were determined to be  $n = 0.770$  (limits 0.692–0.845) and  $n = 0.565$  (limits 0.481–0.649) for the untreated and the *O*-methylated samples, with particle size 80–100  $\mu\text{m}$ , respectively. In addition, methylation of the hydroxyl and carboxylic groups changed the state of the coal sample from glassy to rubbery

TABLE III  
Values of the Exponent in the Semi-empirical Transport Eq. (1):  
Data Set 5 on PSOC-207, 79.82% C (dmmf)

Sample condition	Particle size (mesh)	$n \pm SD$	No. of points	Transport mechanism	Multiple $r^2$
Untreated	20–30	$0.840 \pm 0.026$	17	Case-II	0.986
Untreated	80–100	$0.700 \pm 0.039$	14	Anomalous	0.970
Pyridine-extracted	20–30	$0.629 \pm 0.030$	9	Anomalous	0.985
Air-oxidized	20–30	$0.886 \pm 0.031$	18	Case-II	0.981
<i>O</i> -methylated	80–100	$0.565 \pm 0.042$	19	Anomalous	0.913



TABLE IV  
Results from Transport Analysis with Relaxation Eq. (3):  
Data Set 5 on PSOC-207, 79.82% C (dmmf)

Sample condition	Particle size (mesh)	Relaxation constant <sup>a</sup> $\times 10^{-4}$	No. of points	Equilibrium <sup>b</sup> concentration	Multiple $r^2$
Untreated	20-30	$2.072 \pm 0.036$	18	0.798	0.995
Untreated	80-100	$1.168 \pm 0.043$	15	0.814	0.983
Pyridine-extracted	20-30	$7.318 \pm 0.310$	10	1.065	0.985
Air-oxidized	20-30	$1.985 \pm 0.050$	19	0.801	0.989

<sup>a</sup>Relaxation constant units are g pyridine per hr per surface area in  $\text{cm}^2 \pm$  standard deviation.

<sup>b</sup>Equilibrium concentration units are g pyridine per  $\text{cm}^3$  coal.

material. These results indicate that the Liotta methylation technique degraded the coal network leading to an almost Fickian pyridine diffusion.

Air oxidation appears to have rendered the coal sample PSOC-207 (with particle size 20-30 mesh) more glassy, as the value of the exponent changed from  $n = 0.840$  (limits 0.789-0.893) for the untreated sample to  $n = 0.886$  (limits 0.824-0.948) after oxidation. Such results are consistent with data presented by Green et al.,<sup>2</sup> where it was shown that extensive air oxidation shifted the temperature range of coal fluidity upward.

Pyridine extraction of the coal sample had a less conclusive effect on the mechanism of pyridine transport in coal. For sample PSOC-207, the value of  $n$  decreased from 0.840 before extraction to 0.629 after extraction, for particles of 20-30 mesh size. However, for sample PSOC-212, the value of  $n$  increased from 0.784 to 1.210 after extraction. Clearly then, during pyridine extraction smaller molecular weight aliphatic chains are removed from the coal network. This removal may affect the nature of the pyridine transport mechanism. In fact, the recent studies of Hill-Lievense et al.<sup>31</sup> have shown that this is a possible mechanism. This phenomenon may be also explained as a crude indication of consolidation phenomena in pretreated glassy samples as suggested by Ensore et al.<sup>29</sup> Of course, such an assertion is difficult to prove with such heterogeneous systems as coal networks.

## CONCLUSIONS

In conclusion, we have shown that dynamic swelling of the macromolecular structure of bituminous coals leads to important information about this structure. Pyridine transport at 35°C seems to be controlled by the macromolecular relaxations which become more prominent in oxidized samples and almost disappear in degraded (*O*-methylated) samples.

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