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## PENETRANT TRANSPORT IN COAL NETWORK STRUCTURES BETWEEN 35°C AND 150°C

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Keyword: coal network, penetrant transport, Case-II transport

### INTRODUCTION

The dynamics of penetrant swelling of macromolecular coal systems can provide important information about the structure of the coal itself and its interactions with vapors and liquids. For example, it is possible to identify the thermodynamic state of the coal network. Inflections or dips in the time-sorption curve may be attributed to specific relaxations of the macromolecular coal system. If the coal is in the glassy state, one can determine whether the sorption is due to Fickian diffusion and/or due to relaxations of the macromolecular coal chains and estimate values of the diffusion coefficient and of the relaxation constants.

Increased concentration of penetrant in a macromolecular coal system has the same effect as increase of the temperature. As sorption continues, the density of the coal decreases thus allowing increased bond rotations and mobility. In addition, the favorable energetics involved in sorption provide the energy required for motion. Thus the glass transition temperature is lowered by the presence of the penetrant.

In previous work from our laboratory (1-7) we have examined the mechanism of penetrant transport in coal networks at low temperatures using pyridine (1-6) and various other amines (7). We have concluded that at low temperature (below 50°C) the mechanism of pyridine transport is non-Fickian or Case-II and that the size of the samples tested may shift the overall coupling of the diffusional and relaxational mechanisms.

Analysis of the sorption data can be accomplished by various means. For example, a convenient method of analysis involves fitting of the sorption data (4) 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 systems. For a thin slab, when  $n$  equals 0.5, the diffusion is Fickian. When  $n$  is 1.0, Case II transport occurs. Finally, values of  $n$  between 0.5 and 1.0 indicate anomalous transport. If  $n > 1.0$ , the swelling material is likely to craze and fracture due to the tremendous osmotic pressure differences at the accelerating and advancing front. This type of transport mechanism is known as Super Case II transport.

\* Correspondence



Up to now only one research contribution from our laboratory (8) has examined the change in temperature as a method to decouple the diffusion and relaxation phenomena. In the present work we examine the transport of various penetrants in coal sections at moderate temperatures.

## EXPERIMENTAL PART

Coal samples were supplied by the Pennsylvania State University Coal Bank (PSU). Table 1 includes pertinent information provided by PSU for the coals used in this investigation.

Table 1. Analysis of Coal Samples Used

PSOC Code No.	County, State	Rank	%C (dmmf)	%H (dmmf)	%MM (dry)
418	Titus, TX	LigA	69.9	6.1	27.5
791	Titus, TX	LigA	72.2	5.3	20.7
247	Burke, ND	LigA	75.5	4.8	12.7
312	Navajo, AR	HVC	78.3	5.7	7.5
853	Delta, CO	HVC	80.1	5.0	3.7
402	Craig, OK	HVA	82.4	5.6	18.4
341	Jefferson, PA	HVA	86.0	5.7	14.5
384	Sullivan, PA	SAn	94.1	3.5	24.1

The techniques presented here for preparing uncontaminated thin section specimens of coal are based on the method of preparation employed by Brenner (9). Uncontaminated coal samples were prepared using a paraffin-based adhesive which could be completely removed from the sample. A chunk of coal was ground flat in a direction parallel to the geographic bedding plane on a horizontal diamond grinding wheel using progressively finer diamond grits. The flat surface of the coal was then heat cemented to a pre-conditioned microscope slide. When the hexane-soluble, paraffin-based, thermoplastic adhesive (Paraplast, American Scientific Products) had hardened, the coal chunk was cut with a diamond saw leaving approximately a two millimeter thick slab of coal mounted on the glass slide. The slab was then ground using a vertical diamond grinding wheel to the desired final thickness. The thin section specimens of coal were removed from the glass slide by soaking in n-hexane for several hours. Hexane did not swell the coal sample. After a few days of immersion, the solvent was removed, the samples were oven-dried at 60°C and stored in a dry nitrogen atmosphere at room temperature until use. The uncontaminated samples obtained ranged in thickness from 100  $\mu\text{m}$  to 1500  $\mu\text{m}$ . Thin coal sections, 200  $\mu\text{m}$  to 1200  $\mu\text{m}$  thick, of 1 mg to 10 mg were dried and cut in squares. They were introduced to one of the chambers of a thermogravimetric analyzer (TGS-2, Perkin Elmer, Norwalk, Connecticut) and the whole system was calibrated. The electrobalance system of the TGS-2 was purged with a continuous stream of nitrogen passing through three traps filled with N,N-dimethyl formamide (DMF) or pyridine. By adjusting the flow rate of nitrogen it was possible to control the evaporation rate of DMF or pyridine and, therefore, the ratio in the gaseous phase. Therefore, it was possible to conduct dynamic DMF uptake experiments at different activities. In addition, because of the microfurnace available in the thermogravimetric system, it was possible to carry out experiments at various temperatures.

## RESULTS AND DISCUSSION

Selected data of pyridine and DMF uptake as a function of time and temperature are presented in Figures 1 through 6. In all cases, the diffusion time has been normalized with respect to the square of the sample thickness,  $t/l^2$ . In addition, all graphs present the amount of penetrant adsorbed per gram of dry coal,  $M_t/M_c$ .

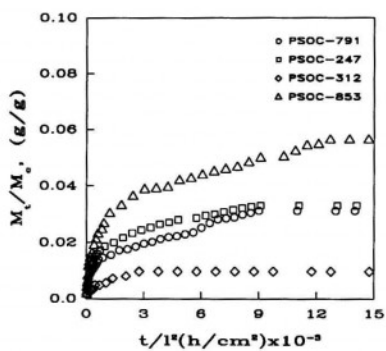


Fig. 1. Pyridine uptake in thin coal sections at 35°C.

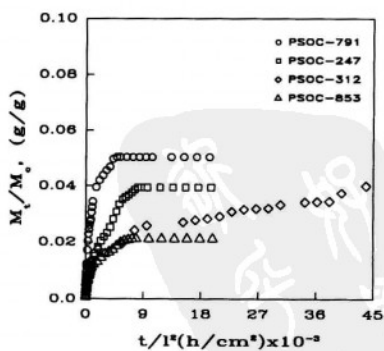


Fig. 2. Pyridine uptake in thin coal sections at 100°C.

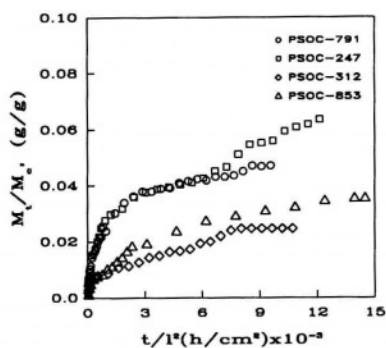


Fig. 3. Pyridine uptake in thin coal sections at 150°C.

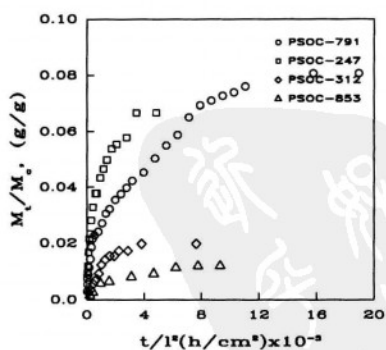


Fig. 4. DMF uptake in thin coal sections at 35°C.

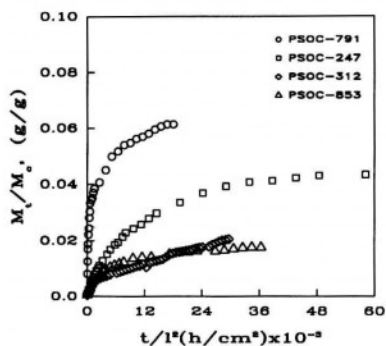


Fig. 5. DMF uptake in thin coal sections at 100°C.

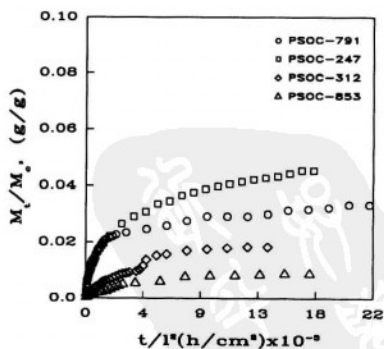


Fig. 6. DMF uptake in thin coal sections at 150°C.

These results were analyzed using equation (1) and the value of k and n are reported in Tables 2 and 3, respectively.

Table 2  
Analysis of Pyridine Uptake by Coal Samples Using Equation (1)

PSOC	Temperature (°C)	n	95% CI for n	k	95% CI for k
791	35	0.42	0.06	$8.6 \times 10^{-4}$	$2.3 \times 10^{-4}$
247	35	0.56	0.05	$4.3 \times 10^{-4}$	$1.1 \times 10^{-4}$
312	35	0.34	0.12	$5.1 \times 10^{-4}$	$2.6 \times 10^{-4}$
853	35	0.61	0.09	$4.6 \times 10^{-4}$	$2.0 \times 10^{-4}$
-	-	-	-	-	-
791	100	0.47	0.04	$1.2 \times 10^{-3}$	$2.4 \times 10^{-4}$
247	100	0.61	0.03	$1.8 \times 10^{-4}$	$3.3 \times 10^{-5}$
312	100	0.32	0.04	$1.4 \times 10^{-3}$	$3.5 \times 10^{-4}$
853	100	0.68	0.09	$1.2 \times 10^{-4}$	$4.4 \times 10^{-5}$
-	-	-	-	-	-
791	150	0.41	0.02	$1.4 \times 10^{-3}$	$1.4 \times 10^{-4}$
247	150	0.58	0.08	$6.9 \times 10^{-3}$	$2.8 \times 10^{-3}$
312	150	0.32	0.04	$4.2 \times 10^{-2}$	$9.1 \times 10^{-3}$
853	150	0.61	0.09	$4.2 \times 10^{-3}$	$2.0 \times 10^{-3}$

Table 3  
Analysis of DMF Uptake by Coal Samples Using Equation (1)

PSOC	Temperature (°C)	n	95% CI for n	k	95% CI for k
791	35	0.49	0.05	$8.8 \times 10^{-4}$	$2.4 \times 10^{-4}$
247	35	0.51	0.04	$1.5 \times 10^{-3}$	$2.9 \times 10^{-4}$
312	35	0.74	0.13	$6.5 \times 10^{-5}$	$3.6 \times 10^{-5}$
853	35	0.62	0.29	$6.6 \times 10^{-5}$	$5.6 \times 10^{-5}$
-	-	-	-	-	-
791	100	0.47	0.07	$1.6 \times 10^{-3}$	$5.5 \times 10^{-4}$
247	100	0.67	0.03	$5.7 \times 10^{-5}$	$1.0 \times 10^{-5}$
312	100	0.52	0.03	$9.6 \times 10^{-5}$	$1.7 \times 10^{-5}$
853	100	0.70	0.04	$3.3 \times 10^{-5}$	$8.3 \times 10^{-6}$
-	-	-	-	-	-
791	150	0.59	0.06	$3.2 \times 10^{-4}$	$9.5 \times 10^{-5}$
247	150	0.55	0.03	$3.9 \times 10^{-4}$	$7.1 \times 10^{-5}$
312	150	0.61	0.02	$6.7 \times 10^{-5}$	$9.9 \times 10^{-6}$
853	150	0.65	0.04	$2.4 \times 10^{-5}$	$5.2 \times 10^{-6}$

These results indicate that anomalous transport is observed in some samples of coal, especially at the higher degree of crosslinking, exemplified by the high carbon content of the coal samples. No Case-II transport was observed, and the results indicate a slight decoupling of diffusion and relaxation at higher temperatures.

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## The Relationships Between Coal Macromolecular Structure and Solvent Diffusion Mechanisms

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**Key Words:** Macromolecular structure, diffusion, viscoelastic properties

### Introduction

The diffusion of solvents through coal is the limiting step of many coal processes and measurement of the mechanism and kinetics of solvent diffusion has been the subject of numerous investigations<sup>1,2</sup>. It is generally accepted that solvent diffusion through coal is analogous to the diffusion of solvents through conventional glassy polymers and much of the formalism of the latter has been applied to coal<sup>3</sup>. The diffusion of solvents may vary between two extrema. If the diffusion is controlled by the concentration gradient between the center and the outside of the particle the diffusion mechanism is Fickian and, for diffusion into a sphere, the kinetics are expressed by the following expression<sup>4</sup>:

$$\frac{M(t)}{M_e} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp(-Dn^2 \pi^2 t/a^2) \quad 1$$

where  $M(t)$  is the mass uptake at time  $t$ ,  $M_e$  is the equilibrium mass uptake,  $a$  is the particle radius and  $D$  is the diffusion coefficient. However, the mechanism of diffusion can deviate significantly from the Fickian mode when the diffusing solvent changes the viscoelastic properties of the glassy solvent. In the limit the diffusion of solvents is completely controlled by polymer relaxation and the solvent advances through the polymer with a well defined front such that ahead of the front the solvent concentration is zero and behind the front the solvent is at equilibrium concentration. Furthermore, ahead of the front the polymer is glassy and behind the front the solvent is rubbery. This kind of diffusion is referred to as "relaxation" or "Case II" diffusion and is characterized either by a polymer relaxation constant or the front velocity. Simple integration of the mass uptake at time  $t$  gives the following kinetic expression<sup>5</sup>:

$$\frac{M(t)}{M_e} = 1 - (1 - k_0 t / C_0 a)^3 \quad 2$$

where  $k_0$  is the relaxation constant and  $C_0$  is the equilibrium solvent concentration. The

front velocity is  $k_0/C_0$ .

Diffusion mechanisms for solvents through coals has been shown to vary between these limits<sup>2</sup>. However, the structural features of the coal macromolecular structure or the details of the macromolecular/solvent interactions which determine diffusion mechanisms remain undefined and are the subject of this paper.

The method used to monitor the amount of solvent that has diffused into the solvent is Dynamic Volumetric Swelling (DVS). Essentially, the amount of volumetric swelling is monitored as a function of time. Only solvent that has diffused into the "bulk" structure can cause coal to swell so that this technique is insensitive to occluded solvent. At any time  $T$ , the amount of solvent that has diffused into the bulk is proportional to the amount of volumetric swelling, so that:

$$\frac{M(t)}{M_e} = \frac{Q(t)}{Q_e} \quad 3$$

where  $Q(t)$  is the amount of volumetric swelling at time  $t$  and  $Q_e$  is the equilibrium swelling. Graphically, to distinguish between the extremal modes of diffusion it is conventional to plot the normalized mass (or swelling) uptake as a function of root normalized time,  $(t/t_e)^{1/2}$ . Figure 1 shows the normalized plots for the theoretical Fickian and Relaxation diffusion modes. It can be seen that under this regime the normalized Fickian curve increases monotonically whereas the Relaxation controlled mode has an inflexion at low  $(t/t_e)^{1/2}$ .

### Experimental

The apparatus was adapted from a design by Aida and Squires<sup>6</sup>. Essentially it consists of a glass cylinder 2 cm in diameter in which coal, supported by a quartz frit, interacts with the solvent. A light PTFE piston is placed on top of the coal and the increase in the height of the coal sample is monitored by a linear transducer connected to a microcomputer. The piston was of such a size as to allow a gap of about 1/4mm between the itself and the outer cylinder. The reaction chamber was surrounded by a constant temperature water bath, kept at 313K for these experiments. The coals were ground to between 60 and 30 Tyler mesh. With this particle size the diffusion of solvents through the coal bed was at least two orders of magnitude faster than diffusion into the particles. Coal was placed into the cylinder and the upper surface levelled. The initial height of the coal sample was measured and the piston and transducer placed on the coal. Solvent was introduced into the chamber to just below the frit and allowed to come to thermal equilibrium. Further solvent was added until the coal and piston were covered. The increase in sample height was monitored as a function of time. Since the approach to equilibrium swelling was asymptotic, the equilibrium time was chosen as the time to reach 99.5% of the equilibrium swelling value.

The coals were obtained from the coal bank of the Northern Carbon Research Laboratories and are described in Table 1. Two solvent sets were chosen, a set of



substituted pyridine molecules and a set of straight chain amines. The former were chosen because the steric properties of the molecules are similar but the basicity depends upon the substitution. In the latter, the molar volume increases with amine chain length whereas the basicity is relatively constant with amine chain length. The  $pK_b$  values and molar volumes of these solvent sets are given in Table 2.

## Results and Discussion

Figure 2 shows the swelling curves for Gedling coal as a function of time. As would be expected, the time to equilibrium swelling (as defined above) increases as a function of amine chain length or molar volume. The amount of swelling also increases with amine molar volume, as observed by Green and West<sup>7</sup>. However, Figure 3 shows that when the swelling is normalized and plotted against root normalized time the curves have the same trajectory. Therefore all of the amines have the same swelling mechanism, regardless of molar volume.

Figure 4 shows the normalized DVS data for the substituted pyridine set. The diffusion changes from an anomalous mode for the pyridine and 2-methylpyridine to Fickian for the 2-fluoropyridine.

The principal mechanism of swelling for bases such as the amine and substituted pyridine sets appears to involve the disruption of inter chain hydrogen bonds<sup>8,9</sup>. Coal hydrogen bonds have a range of bond energy<sup>9</sup>. One result of this is that weaker bases, such as the 2-fluoropyridine, are able to disrupt only the weakest hydrogen bonds, stronger hydrogen bonds act as *de facto* crosslinks. As solvent basicity increases in the substituted pyridine set the solvents are able to disrupt increasing numbers of hydrogen bonds. Eventually a point is reached at which all of the hydrogen bonds are disrupted. This is manifested as a plateau in swelling/basicity curves<sup>9</sup>.

One explanation of the progressive change from anomalous diffusion to Fickian diffusion could be that as the bases disrupt hydrogen bonds so the viscoelastic properties of the coals change from glassy to increasingly rubbery in the presence of the solvents. However, Figure 4 shows that pyridine and 2-methylpyridine have the same diffusion mechanism, even though their basicities are significantly different. This can be rationalized by noting that pyridine and 2-methylpyridine swell Gedling coal to the same extent<sup>9</sup> and, by hypothesis, disrupt the same number of hydrogen bonds.

Further corroborative evidence for the above theory comes from the diffusion mechanisms of the straight chain amine set. The amine chain length has little effect on molecular basicity and the observed increase in swelling with chain length has been attributed to the presence of increasingly larger molecules within the coal structure<sup>7</sup>. Green and West<sup>7</sup> have presented evidence to suggest that the molar amount of amine is absorbed per unit weight of coal is independent of amine size. This is consistent with the idea of