

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_∞ 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.

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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 μm to 1500 μm . Thin coal sections, 200 μm to 1200 μm 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 .

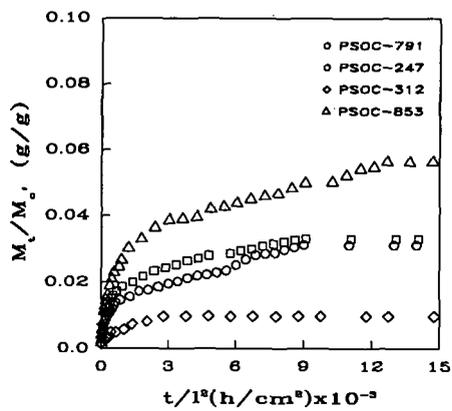


Fig. 1. Pyridine uptake in thin coal sections at 35°C.

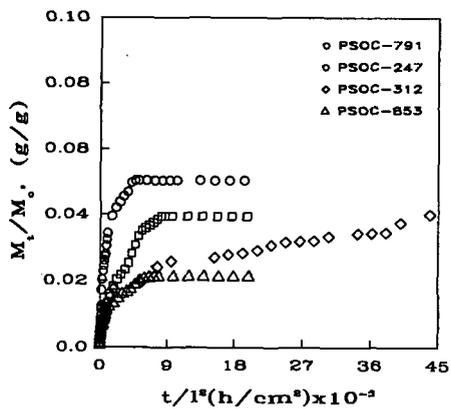


Fig. 2. Pyridine uptake in thin coal sections at 100°C.

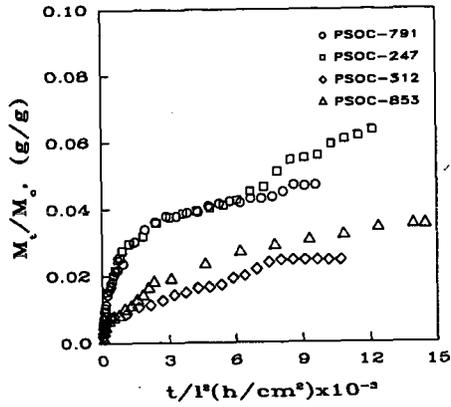


Fig. 3. Pyridine uptake in thin coal sections at 150°C.

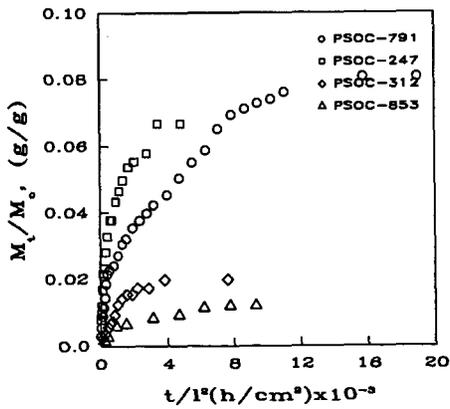


Fig. 4. DMF uptake in thin coal sections at 35°C.

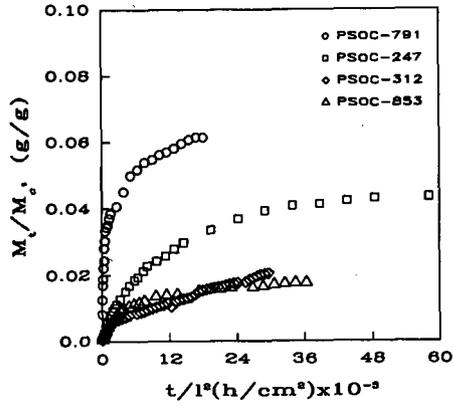


Fig. 5. DMF uptake in thin coal sections at 100°C.

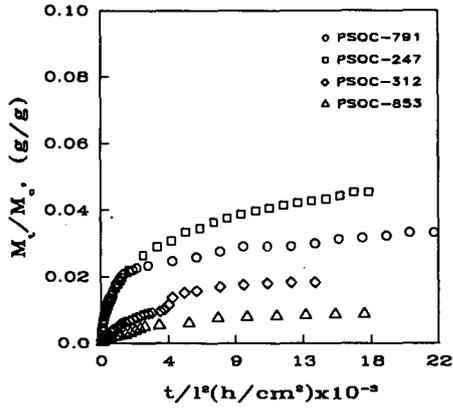


Fig. 6. DMF uptake in thin coal sections at 150°C.

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	8.6×10^{-4}	2.3×10^{-4}
247	35	0.56	0.05	4.3×10^{-4}	1.1×10^{-4}
312	35	0.34	0.12	5.1×10^{-4}	2.6×10^{-4}
853	35	0.61	0.09	4.6×10^{-4}	2.0×10^{-4}
-	-	-	-	-	-
791	100	0.47	0.04	1.2×10^{-3}	2.4×10^{-4}
247	100	0.61	0.03	1.8×10^{-4}	3.3×10^{-5}
312	100	0.32	0.04	1.4×10^{-3}	3.5×10^{-4}
853	100	0.68	0.09	1.2×10^{-4}	4.4×10^{-5}
-	-	-	-	-	-
791	150	0.41	0.02	1.4×10^{-3}	1.4×10^{-4}
247	150	0.58	0.08	6.9×10^{-3}	2.8×10^{-3}
312	150	0.32	0.04	4.2×10^{-2}	9.1×10^{-3}
853	150	0.61	0.09	4.2×10^{-3}	2.0×10^{-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	8.8×10^{-4}	2.4×10^{-4}
247	35	0.51	0.04	1.5×10^{-3}	2.9×10^{-4}
312	35	0.74	0.13	6.5×10^{-5}	3.6×10^{-5}
853	35	0.62	0.29	6.6×10^{-5}	5.6×10^{-5}
-	-	-	-	-	-
791	100	0.47	0.07	1.6×10^{-3}	5.5×10^{-4}
247	100	0.67	0.03	5.7×10^{-5}	1.0×10^{-5}
312	100	0.52	0.03	9.6×10^{-5}	1.7×10^{-5}
853	100	0.70	0.04	3.3×10^{-5}	8.3×10^{-6}
-	-	-	-	-	-
791	150	0.59	0.06	3.2×10^{-4}	9.5×10^{-5}
247	150	0.55	0.03	3.9×10^{-4}	7.1×10^{-5}
312	150	0.61	0.02	6.7×10^{-5}	9.9×10^{-6}
853	150	0.65	0.04	2.4×10^{-5}	5.2×10^{-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.

This work was supported by a grant from the Department of Energy (PETC).

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