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Solvent Swelling of Maceral Concentrates

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The volumetric swelling ratios of three coals and their maceral concentrates in the presence of pyridine were determined by the displacement of a piston and by the measurement of swollen and unswollen particle size distributions using a laser diffraction particle size instrument. The use of particle size distributions allows the measurement of swelling ratios without the possible problems of changes in particle packing associated with the piston apparatus. The piston apparatus, however, has the advantage that the kinetics of solvent uptake can be evaluated. Equilibrium swelling ratios were generally found to increase in the order vitrinite > liptinite > inertinite, which implies that the apparent cross-link density increases in the order inertinite > liptinite > vitrinite. Extracted coals and maceral concentrates were found to have greater swelling ratios than raw coal samples.

Introduction

The macromolecular structure of coal has been of considerable interest to coal scientists because of its potential importance in the characterization of coal for utilization. Coal consists of polynuclear aromatic and hydroaromatic clusters cross-linked by covalent bonds, hydrogen bonds, and weak intermolecular interactions to give a three-dimensional network. The degree of cross-linking has been related to the thermoplastic properties of coal and is a major factor in the determination of mechanical properties.¹

A strongly basic solvent such as pyridine disrupts cross-linking hydrogen bonds in coal by replacing them with solvent–coal hydrogen bonds. Reorientation of the macromolecular clusters occurs, resulting in the volumetric swelling of the coal. The macromolecular clusters obtain a high mobility by removal of the coal–coal hydrogen bonds, and the coal becomes rubbery.² The volumetric swelling ratio, Q_v , is the ratio of swollen volume (at equilibrium) to initial volume. Q_v is equal to the reciprocal of the volume fraction of polymer chains in the swollen sample as given by the Flory–Rehner theory.^{3,4} Solvent swelling behavior has been used to give a measure of the apparent cross-link density of coal.^{5,6} The maximum amount of swelling possible is limited by the number of covalent cross-links.^{7,8} The degree of solvent swelling that takes place is a measure of the compatibility of the solvent–coal interaction and the ease of displacement of the cross-linkages,⁶ which is dependent on the enthalpies of the interactions involved.⁹ The swelling ratio is a function of the basicity

of the solvent,^{8,10} increasing with increasing basicity until reaching a plateau at $pK_b \sim 9$. Since coals contain hydrogen bonds with a range of bond enthalpies,⁵ solvents with a high electron donating capacity (which is related to basicity⁹) will disrupt a greater number of the cross-linking coal–coal hydrogen bonds. The molecular size of the solvent also affects the degree of swelling.^{9,11}

Within the coal network a complex mixture of relatively low molecular weight material is physically trapped or weakly bonded to the macromolecular structure; the nature of this material has been the subject of extensive debate.^{12–14} Nishioka¹⁵ has argued that a significant proportion of coal exists as an associated molecular structure, with associative equilibria existing between the extractable molecules and coal molecules. It was suggested that the associations were held together by relatively strong secondary interactions. Solvent-induced association was found to be possible between coal and its extract with solvent treatment (immersion in a good solvent), resulting in decreased extractability and solvent swelling.¹⁵ Nishioka and Larsen¹⁶ found that by heating coal in a slightly polar solvent (chlorobenzene) to 115 °C there was a decrease in solvent extraction yields. It was suggested that the solvent acted as a plasticizer at the higher temperatures, overcame activation barriers to molecular motion, and allowed the formation of lower energy configurations via association by secondary interactions.

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The secondary interactions occur in coals of all ranks; however, the reversibility of swelling has a rank dependency.¹⁵ Thermally induced dissociation of extractable molecules takes place during Soxhlet extraction with pyridine, with higher temperatures increasing the amount of extractable material.¹⁶ Since hydrogen bonds are disrupted by pyridine, the additional extraction was suggested to be due to the thermal dissociation of polarizable aromatic π system interactions. The presence of soluble material does not significantly affect solvent activity,¹⁷ although low coal to solvent ratios resulted in greater swelling due to an increase in the amount of secondary interactions solvated. Apparent cross-link densities calculated from swelling ratios may contain contributions from both relatively strong secondary interactions and covalent bonding.¹⁸

Green and Larsen⁷ have suggested that pyridine extraction alters the macromolecular structure of coal by reducing the number of noncovalent cross-links, since not all of the hydrogen bonds re-form on pyridine removal. The extractable component of coal is clearly held in the macromolecular structure by a variety of site specific interactions. Marzec and Kisielow¹⁹ concluded that the extractable fraction is bound to the macromolecular structure by electron donor-acceptor interactions. Pyridine, while disrupting the hydrogen bonds in the structure, may not completely disrupt all interactions between the molecular phase and the macromolecular structure or all noncovalent cross-links of the macromolecular structure itself.

Coal macerals have distinct chemical and physical characteristics;²⁰ however, with the exception of vitrinite, there has been little previous work on the solvent swelling of macerals, and few workers consider maceral composition as a major factor in swelling studies. In an early study Bunte *et al.*²¹ measured the gravimetric adsorption of pyridine for the lithotypes of Hernitz coal (84.5% C). The coal swelled to a greater extent than vitrain, fusain, or durain lithotypes, with fusain showing the least response to the solvent. It was noted that durain did not fit into an observed relationship with C/H ratio in which swelling decreased with increasing C/H. The discrepancy was thought to be due to the high volatile matter content of the durain, presumably due to the higher amount of liptinic material. The results obtained by Bunte *et al.* were thought to be unusually low,²² and there are uncertainties concerning lithotypes from different parts of the seam; however, the influence of petrographic composition cannot be ignored.

The degree of swelling of a high volatile bituminous coal was investigated by Shibaoka *et al.*²³ using optical microscopy. Vitrinite was reported to swell after exposure to pyridine, while liptinite and inertinite macerals were little affected with the possible exception of low-reflecting semi-fusinite. Brenner²⁴ also conducted a microscopic examination of coal swelling. Swelling was

reported to be reversible if the solvent was removed early on; however, on prolonged swelling the reversibility was progressively lost. The irreversibility was due to fracturing of the coal due to differential swelling, which was suggested to be caused mainly by faster expansion of the outer region of the coal with differential swelling of the microscopic constituents (macerals) as a secondary cause.

The evidence for differences in the swelling ratios of macerals indicates that the macromolecular structures of macerals from the same coal are different. This has important implications in the way that solvent swelling studies are conducted if it holds true for coals of different ranks and maceral compositions. The aim of this investigation was to compare the solvent swelling ratios of maceral concentrates to the corresponding whole coals both before and after extraction with pyridine to determine whether there were any consistent patterns.

Experimental Section

Maceral Group Concentrates. Three coals, Sierza (S) and Kellingley (K), from the SBN Coal Bank, and Daw Mill (D), from the CRE Coal Bank, were selected for separation into vitrinite, liptinite, and inertinite maceral group concentrates. The coal samples were reduced to $-75\ \mu\text{m}$ and chemically demineralized using HCl and HF. A fluid energy mill was then used to produce micronized coal with an average particle size of $3\ \mu\text{m}$. Density profiles of the coals were obtained using the density gradient centrifugation (DGC) technique²⁵⁻²⁸ on a 2 g sample of each coal by the Maceral Separation Laboratory, Southern Illinois University. Density cut points were then selected using the DGC profiles obtained and, where necessary, petrographic analysis of the separated DGC fractions. Sink-float separations using aqueous CsCl solutions with added surfactant (Brij-35) were then carried out to obtain the maceral group concentrates. The samples were rinsed with dilute HCl followed by distilled water, since this procedure was more efficient at removing CsCl than water alone. The purity of the separated macerals were determined by a point count of a minimum of 500 particles, using the reflectance as a guide to maceral identification. Typical theoretical standard deviations for maceral composition values are ± 1 for the concentrates. The petrographic and chemical analyses of the whole coals and the maceral concentrates are given in Tables 1 and 2, respectively.

Pyridine-Extracted Samples. Pyridine extraction of the samples was carried out using a Soxhlet apparatus until the liquid in the siphon tube ran clear. This usually occurred within 24 h due to the small sample size used and the small particle size of the samples. The samples were then vacuum dried overnight in a desiccator prior to swelling. The density of the extracted samples was determined by sink-float techniques using aqueous CsCl solutions with the aid of a centrifuge and were found to not vary greatly from the raw macerals. Due to limitations on the amount of material available, extracted samples were produced from raw maceral concentrates used previously for solvent swelling studies.

Solvent Swelling Using Piston Apparatus. The solvent swelling apparatus used in the experiments was based on that used in previous studies^{29,30} in which swelling of a sample is followed by the linear displacement of a piston placed on top of a coal sample. A 9 mm diameter glass sample cell with a

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Table 1. Petrographic Analysis of Whole Coals and Their Maceral Group Concentrates

coal	sample	density, g cm ⁻³	maceral group analysis, vol % mmf			vitrinite reflectance <i>R</i> ₀ , % _{random}
			liptinite	vitrinite	inertinite	
Sierza	whole coal		23	50	26	0.50 ± 0.10
	liptinite	<1.25	93	6	1	
	vitrinite	1.35–1.45	1	87	12	
Daw Mill	whole coal		14	62	27	0.56 ± 0.07
	liptinite	<1.24	74	24	2	
	vitrinite	1.24–1.39	5	88	7	
	inertinite	1.39–1.6	1	4	95	
Kellingley	whole coal		14	72	14	0.68 ± 0.06
	liptinite	<1.17	94	4	2	
	vitrinite	1.17–1.31	3	95	2	
	inertinite	1.31–1.7	3	24	73	
Wearmouth	whole coal		12	74	14	0.85

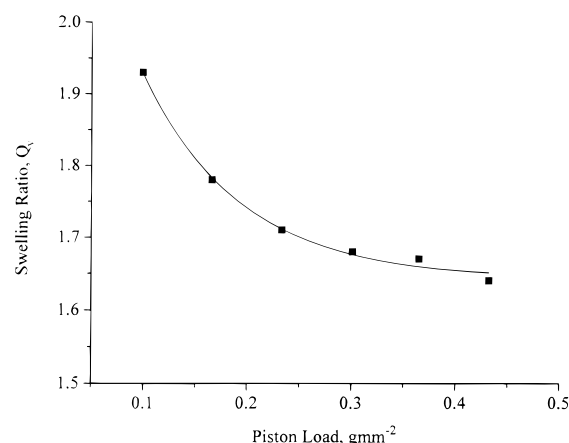
Table 2. Proximate and Ultimate Analyses of Whole Coal Samples (Demineralized unless Otherwise Stated) and Their Maceral Group Concentrates

coal	sample	proximate analysis, wt % db			ultimate analysis, wt % db		
		volatile matter	fixed C	ash	C	H	N
Sierza	whole coal	39.5	57.3	3.2	77.6	4.1	1.2
	vitrinite	41.5	56.0	2.5	75.9	4.3	1.2
	liptinite	68.2	29.7	2.1	78.1	7.0	1.2
Daw Mill	whole coal	39.8	57.6	2.7	78.5	4.9	1.2
	whole coal ^a	38.8	52.7	8.5	78.1	4.8	1.2
	vitrinite	40.6	55.3	4.2	78.5	4.8	1.0
	liptinite	54.5	37.3	8.2	83.9	6.6	0.8
	inertinite	28.4	67.9	3.7	82.8	3.7	1.0
Kellingley	whole coal	39.9	57.1	3.5	81.5	5.0	1.8
	vitrinite	42.2	55.8	2.1	80.3	6.1	1.9
	liptinite	62.9	35.8	1.3	82.2	7.5	1.2
	inertinite	29.1	62.7	8.1	89.3	4.4	1.6
Wearmouth	whole coal ^a	36.5	59.8	3.7	81.3	5.0	

^a Not demineralized.

sintered base sits inside a pyridine reservoir vessel, which in turn is located inside a water bath maintained at 20 °C. A quartz filter disk fitted directly on top of the sinter prevented the ingress of fine particles into the sintered base and created an even surface at the base of the sample cell prior to loading of a 0.4 g sample. The sample was then gently compressed in the sample cell to achieve a packing voidage of approximately 0.5 (fractional free volume within a packed bed). The loaded sample cell was then placed within the pyridine reservoir vessel. A PTFE piston connected to the displacement transducer placed on top of the sample measured the increase in the height of the coal bed. The displacement was recorded via an A/D converter until equilibrium was reached, when no further swelling was observed. The coal to solvent ratio used was about 0.8 w/w %. At this level the effect of soluble coal molecules on solvent activity is thought to be small.

The swelling ratios obtained using this method have been found to depend upon the ratio of the piston weight to the area of the sample tube³¹ (i.e. downward pressure on the coal bed) as shown in Figure 1, due to differences in particle packing. Therefore, the swelling ratios obtained using this method are not directly comparable to those obtained in previous studies using this technique. However, the method gives a continuous measurement of swelling with time, allowing the determination of the equilibrium swelling ratio and information on the kinetics of solvent uptake. For the piston solvent swelling apparatus, the results are corrected for differences in initial packing density to a voidage of 0.5 to account for differences in the specific densities of the maceral group concentrates and the correction required to avoid errors due to differences in the packed coal densities described by Nishioka³² using the equation

**Figure 1.** Effect of piston load on Q_v for coal W using the piston solvent swelling apparatus.³¹

$$Q_{ve} = [(\rho_A - \rho_B)/0.5\rho_A](Q_{vme} - 1) + 1 \quad (1)$$

where ρ_A is the apparent density of the sample obtained from aqueous CsCl DGC profiles, ρ_B is the packed bed density of the sample in the sample tube, and Q_{vme} is the measured equilibrium swelling ratio. Since the mass of the piston used was the same for all samples, it is assumed that they reach the same packing densities at the end of the measurement; thus, there is no need to correct for the final voidage. If this assumption is wrong and the final packing achieved is some function of swelling, the value of Q_v obtained will still provide a comparative measure. The repeatability for multiple runs was ± 0.02 after correction using eq 1. The extracted whole coals and maceral concentrates on average were found to have slightly lower average densities (in aqueous CsCl) than the raw samples, although for most samples the change was <0.02 g cm⁻³.

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Solvent uptake follows the generalized empirical expression³³

$$M_t/M_e = kt^n \quad (2)$$

where M_t is the mass uptake of solvent at time t , M_e is the mass of solvent uptake at equilibrium, n is the diffusion exponent, which is indicative of the solvent transport mechanism, and k is a constant. The initial values of n and k can then be obtained.³⁰ Ritger and Peppas³³ determined that for a spherical geometry, Fickian diffusion (which is dependent upon the diffusion coefficient across a concentration gradient), has $n = 0.43$. Case II diffusion, in which diffusion is much greater than the rate of relaxation of the matrix, has $n = 0.85$. Intermediate values correspond to an anomalous diffusion mechanism in which diffusion and relaxation rates are comparable. The degree of swelling is assumed to be proportional to the mass uptake of solvent. The swelling process can then be described by the phenomenological model

$$S_t/S_e = 1 - e^{-kt} \quad (3)$$

where S_t is the swelling volume at time t and S_e is the swelling volume at equilibrium. Hence, a graph of $\ln(1 - S_t/S_e)$ against t gives a straight line with the gradient (k) similar to a rate constant for the swelling process.^{8,10} A graph of $\ln(1 - M_t/M_e)$ against t for Fickian diffusion into a spherical particle also gives a straight line graph for $M_t/M_e > 0.5$.

Swelling Ratios from Particle Size Distributions. Pyridine swelling ratios were also determined from particle size distributions (PSDs) according to the technique described by Turpin *et al.*³⁴ A Fritch Analysette 22E laser diffraction size analyser was used to measure the PSD of coal D maceral samples dispersed in water containing the surfactant Brij-35 and also of samples swollen in pyridine. The samples were placed in a sonic bath for 1 h and left for at least 24 h prior to analysis. Swelling ratios obtained using this method are claimed³⁴ to have the advantage of a high solvent/coal ratio, reducing errors caused by reduced solvent activity due to dissolution of soluble material. Problems caused by changes in the packing voidage that may occur using the piston technique are also eliminated.

Assuming that particles of all sizes swell to the same average extent and that no fracturing or agglomeration occurs, then the swelling ratio can be calculated from any given percentile underclass size.³⁴ The change in the linear dimension of the particle is equal to $\sqrt[3]{Q_v}$. A plot of swollen particle volume against unswollen particle volume at fixed cumulative percentile underclass (10%, 20%, ..., 80%, 90%) is drawn with a best fit line with a forced intercept through the origin of slope Q_v . The volumetric swelling of dry micronized and demineralized coal D in water was determined to be <2% using the piston apparatus. Therefore, there is a small change in volume of the particles when immersed in water (defined as the unswollen particle volume in the PSD method); however, the error in the swelling ratio is very small compared to the swelling in pyridine.

Results

Piston Apparatus. The equilibrium swelling ratios obtained using the piston apparatus for the maceral group concentrates and the whole coals are presented in Tables 3 and 4. The results show that demineralized whole coal samples (before extraction) were found to have a greater equilibrium swelling ratio than any of their maceral group concentrates. For the raw coals, liptinite has a slightly greater swelling ratio than vitrinite in the case of S and K coals, while in the case of coal D, vitrinite swells by a significantly larger amount than liptinite. Inertinite swells the least for

Table 3. Solvent Swelling Ratios, Diffusion Exponents, and Diffusional Rate Constants Obtained Using Piston Apparatus of Coals and Maceral Concentrates before Extraction

coal	sample	Q_{ve}	n^a	k, s^{-1}
Sierza	whole coal	1.34	0.39	2.7×10^{-5}
	liptinite	1.34	1.12	1.3×10^{-3}
	vitrinite	1.33	0.58	6.7×10^{-5}
Daw Mill	whole coal	1.50	0.52	2.0×10^{-4}
	whole coal ^c	1.38		
	liptinite	1.33	0.67	1.2×10^{-3}
	vitrinite	1.48	0.48	4.4×10^{-4}
Kellingley	inertinite	1.32	0.42	1.3×10^{-3}
	whole coal	1.24	0.56	2.6×10^{-4}
	liptinite	1.22	1.40	9.3×10^{-4}
	vitrinite	1.19	0.42	4.2×10^{-4}
	inertinite	1.12	0.45	1.8×10^{-4}

^a From graph of $\ln(S_t/S_e)$ vs $\ln(t)$. ^b From graph $\ln(1 - S_t/S_e)$ vs t . ^c Not demineralized.

Table 4. Solvent Swelling Ratios, Diffusion Exponents, and Diffusional Rate Constants Obtained Using Piston Apparatus for Extracted Coals and Maceral Concentrates

coal	sample	extract yield, %	Q_{ve}	n^a	k, s^{-1}
Sierza	whole coal	11.6	1.45	0.61	3.3×10^{-3}
	liptinite	9.6 ^c	1.36	0.75	1.4×10^{-2}
	vitrinite	5.9 ^c	1.59	0.82	5.5×10^{-3}
Daw Mill	whole coal	14.5, 8.7 ^c	1.58	1.04	2.2×10^{-3}
	liptinite	10.5 ^c	1.39	1.04	1.7×10^{-2}
	vitrinite	10.8, 6.5 ^c	1.64	0.87	9.5×10^{-3}
	inertinite	7.6 ^c	1.24	1.04	1.6×10^{-2}
Kellingley	whole coal	14.7	1.44	0.90	3.6×10^{-3}
	liptinite	11.4 ^c	1.39	0.96	5.8×10^{-3}
	vitrinite	12.6 ^c	1.50	0.79	1.6×10^{-3}
	inertinite	9.5 ^c	1.17	0.98	5.6×10^{-3}

^a From graph of $\ln(S_t/S_e)$ vs $\ln(t)$. ^b From graph $\ln(1 - S_t/S_e)$ vs t . ^c Samples previously swollen in pyridine.

both D and K coals. Micronized coal D, which had not been demineralized, gave a swelling ratio of 1.38, which compares to a ratio of 1.50 for the equivalent demineralized sample. Mineral matter is considered not to swell and corrections for mineral matter may be carried out according to the calculation given by Green *et al.*³⁵ However, since the samples used in this study have low ash contents, the conversion to a mineral matter free basis increases the swelling ratio obtained by only 0.01 for the demineralized samples and by 0.02 for the undemineralized sample. The differences between the samples cannot be attributable to mineral matter effects and are thought to be due to the effect of the demineralization process itself. Similarly, demineralization effects were found using the PSD method as discussed later.

The swelling ratio of demineralized coal K was measured after it had been soaked in 5 M CsCl and 8 g dm⁻³ Brij-35 (used in the separation of the macerals) and washed with concentrated HCl and water (to remove traces of CsCl). A swelling ratio of 1.27 was obtained, representing an increase of 0.03. Although this increase may be due to the effect of residual mineral matter/demineralization, the result is within experimental error and the effect of CsCl treatment on the cross-link density is, therefore, considered to be insignificant.

A comparison of extracted versus raw coal D vitrinite concentrate is shown in Figure 2. The equilibrium

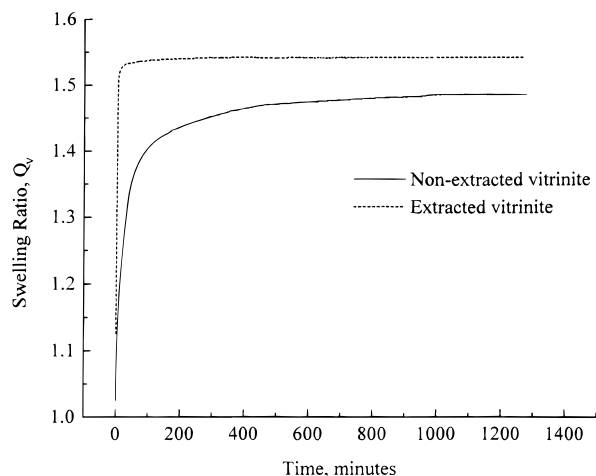


Figure 2. Solvent swelling plot of raw (solid) and extracted coal D vitrinite group concentrate (dotted line).

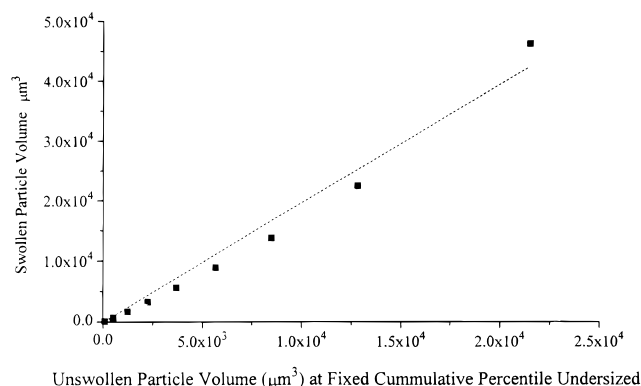


Figure 3. Swollen vs unswollen particle volume for <38 μm undemineralized coal D.

swelling was achieved more rapidly with the extracted sample, although swelling to a greater extent. This is consistent with previous studies.¹⁰ The diffusion exponents and rate constants for solvent uptake are presented in Tables 3 and 4. The raw vitrinite samples have n values of about 0.5, indicative of a Fickian diffusion process. After extraction, the diffusion exponent increased for all samples with the exception of liptinites from coals K and S, with most samples indicating that case II (relaxation) diffusion is important. The average diffusion exponent for the extracted vitrinites for example was 0.83.

Extraction increases the rate constant (k) of solvent uptake. Whole coal samples were generally found to have the lower k values compared to their maceral group concentrates for both extracted and raw coals, with the vitrinite concentrates giving the lowest rate constants for the macerals.

Extract yields for the whole coals are greater than for the maceral concentrates due to the loss of some material from previous swelling tests. The results presented in Table 4 show that extraction increases the solvent swelling equilibrium ratio for all samples with the exception of inertinite D. The greatest increase in the swelling ratio after extraction was for the vitrinite maceral group, while inertinites show the least change. After extraction with pyridine, the swelling ratios increase in the order vitrinite > liptinite > inertinite.

Particle Size Distribution Plots. Graphs of swollen versus unswollen particle volumes are presented in

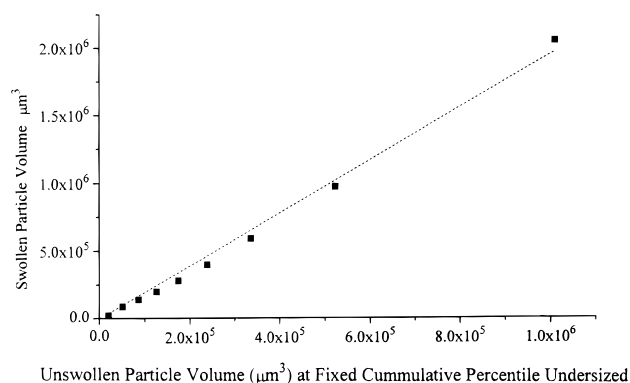


Figure 4. Swollen vs unswollen particle volume for 38–125 μm undemineralized coal D.

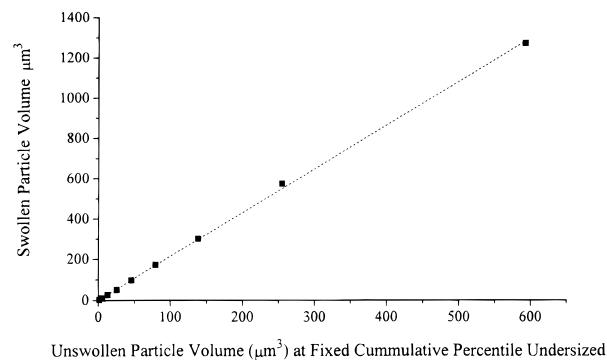


Figure 5. Swollen vs unswollen particle volume for micronized coal D.

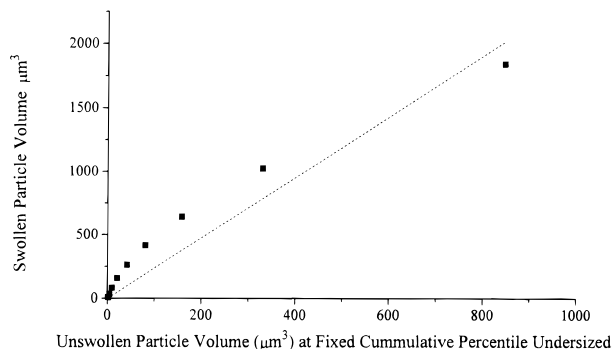


Figure 6. Swollen vs unswollen particle volume for coal D vitrinite.

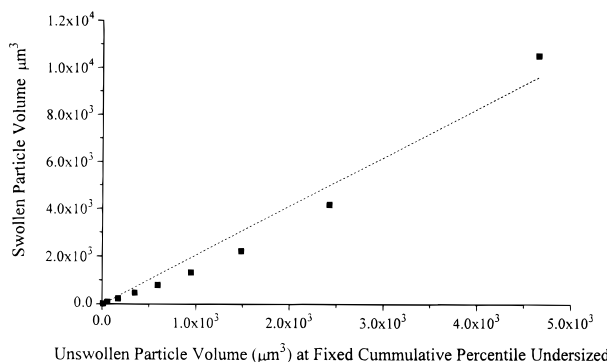


Figure 7. Swollen vs unswollen particle volume for coal D liptinite.

Figures 3–8, from which the swelling ratio was obtained (Table 4). The swelling ratios for whole, raw coal D samples at <38 and 38–125 μm (Figures 3 and 4, respectively) show that there is little variation of Q_v with particle size. Poor results were obtained with this

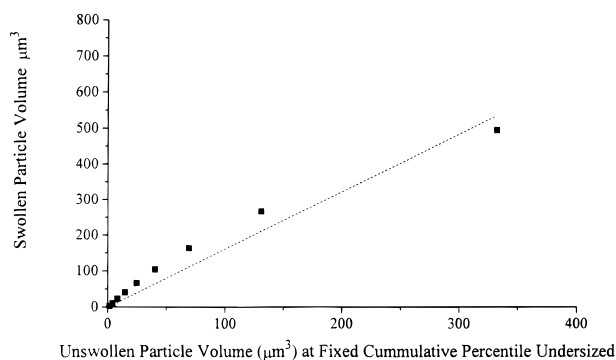


Figure 8. Swollen vs unswollen particle volume for coal D inertinite.

Table 5. Solvent Swelling Ratios from PSDs of Daw Mill Size Fractions and Maceral Concentrates in Water and Swollen in Pyridine

sample	nonextracted Q_{ve}	sample	nonextracted Q_{ve}
<38 μm^a	1.97	liptinite	2.06
38–125 μm^a	1.95	vitrinite	2.38
micronized	2.17	inertinite	1.61

^a Not demineralized.

method for particle sizes above 125 μm , possibly as a result incomplete dispersion of the larger particles in the suspension. Turpin *et al.*³⁴ also experienced difficulties with particle sizes >150 μm ; thus, the use of PSDs to determine swelling ratios seems to be limited to smaller size ranges.

Table 5 shows the swelling ratios obtained from the PSD plots. The swelling ratio for demineralized and micronized whole coal (2.17) was higher than for the <38 and 38–125 μm particle size fractions (swelling ratios of 1.97 and 1.95, respectively). A difference in swelling ratios of 0.02 is directly due to mineral matter effects; thus, the remaining differences of 0.18 and 0.20 are due to the micronization/demineralization process. The comparison of the swelling ratios of micronized coal D, and of the micronized and demineralized coal D obtained using the piston apparatus (see previous section), shows that the demineralization process is responsible for the increase in swelling ratio. The results show very little difference between the swelling ratios of the <38 and 38–125 μm fractions, from which it is concluded that there is negligible size fractionation.

Swelling ratios obtained using the PSDs for the coal D maceral group concentrates increase in the order vitrinite > liptinite > inertinite; whole coal has a Q_v intermediate to those of the vitrinite and liptinite concentrates. The swelling ratios obtained are greater than those obtained from the piston apparatus. The results illustrate that in the piston apparatus the voidage in the packed bed decreases as swelling proceeds; that is, some of the increase in particle volume is accommodated by the free space in the sample cell. In effect, swelling ratios obtained using the PSD method are equivalent to the piston apparatus extrapolated to a piston load of zero using a plot such as that in Figure 1. The ratios obtained from particle size measurements are a true measure of the change in coal volume.

Figures 6–8 show that the data points for liptinite are skewed toward the unswollen axis, while for the inertinites and vitrinites the skew is toward the swollen axis. Turpin *et al.*³⁴ state that if such a skew occurs, then the assumptions that all particles swell to the same

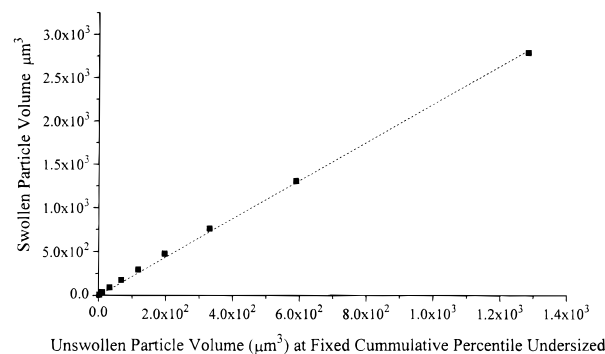


Figure 9. Calculated whole coal from weighted sum of maceral constituents.

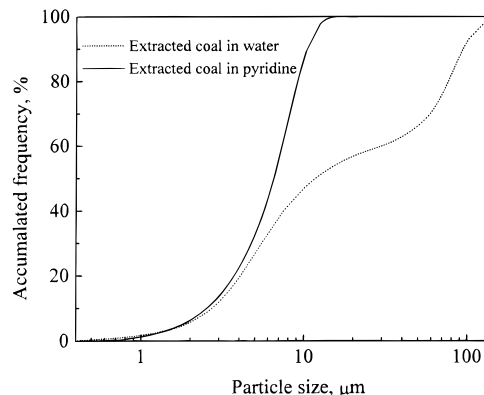


Figure 10. Particle size distributions of pyridine-extracted coal D in water and swollen in pyridine.

average extent irrespective of size, and that no fracturing or agglomeration occurs, have not been met. Since the maceral concentrates are not 100% pure, it may be that some of the larger particles contain a mixture of macerals. It has been shown in the results presented here that macerals swell to different extents; hence, it is apparent that a skewed function may be produced. However, the composite plot (Figure 9) shows the same linearity as that obtained for the micronized whole coal. It is difficult to find a reasonable explanation for this result, although it should be considered that at this particle size the particle analyzer is close to the limits of its resolution.

The PSDs of micronized and extracted coal D in water and pyridine are presented in Figure 10. Similar results were obtained for all of the maceral concentrates obtained from the coal. It can be seen that in water the PSD is bimodal, with particle sizes centered about 6 and 80 μm , whereas in pyridine the particles are distributed about 6 μm only. The results suggest that the micronized particles have agglomerated during the extraction procedure.

Discussion

Similar differences were found between demineralized and undemineralized samples using both the piston and PSD methods, which cannot be attributable to the differences in their mineral matter contents alone. Thus, it is apparent that the demineralization procedure modifies certain interactions in the coal structure. Larsen *et al.*³⁶ have reported the effects of demineral-

(36) Larsen, J. W.; Pan, C.-S.; Shawyer, S. *Energy Fuels* **1989**, *3*, 557.

ization on pyridine swelling ratios for low rank (about 69% C dmmf) coals. Swelling ratios were higher for demineralized coals compared to untreated coals. The demineralized coals also gave higher pyridine extract yields, although higher rank coals showed no increase in extractability on demineralization.³⁶ Nishioka *et al.*³⁷ also found that acid increased pyridine extraction yields, particularly for lignites, with the effect decreasing up to about 84% carbon content, at which no change in yield was found. The treatment of coal in 2 M HCl can lead to higher volatile matter yields during pyrolysis,³⁸ a phenomenon that is reversible by the addition of Ca^{2+} , which indicates that no permanent chemical change occurs. It is thought that acidic groups, such as $-\text{COOH}$ and $-\text{OH}$ which are more abundant at lower ranks, are partially ionized and interact with naturally occurring cations (Ca^{2+} , Na^+ , etc.) in coal. Acid washing strips off the interacting cations, which may then allow the functional groups to form coal-coal bonding upon drying, effectively increasing the noncovalent cross-link density.

To obtain relatively pure maceral concentrates, demineralization is a necessary pretreatment since the macerals are separated on a density basis. However, since the samples have all been through the demineralization procedure, the swelling ratios obtained may be used for comparison purposes with a degree of caution. The effect of CsCl (used in separation) has been determined to be insignificant.

Hall³⁹ investigated the swelling of vitrinite, inertinite, and liptinite concentrates from Rawdon coal (76.3% C dmmf) using a series of solvents increasing in basicity. The results show that the whole coal swelled to the greatest extent at all pK_b values, while vitrinite swelled the least, although it comprised 64% of the whole coal. Inertinite and liptinite swelled to a similar extent. The results obtained using the piston apparatus for the raw coals in this investigation have also shown that the whole coals achieve the highest equilibrium swelling ratio, which indicates that the swelling ratios obtained by the piston method are not additive.

The calculated swelling ratios of raw coals D and K based on the measured swelling ratios of the maceral group concentrates and their maceral compositions are 1.47 and 1.19, respectively. The values are both slightly lower than the measured swelling ratios of the raw coals. The higher swelling ratios for whole coals may be due to the presence of multimaceral particles in the whole coal sample. However, the proposal is not supported by the swelling ratios obtained from PSDs. The calculated swelling ratio for coal D was 2.20, which is not significantly different from the measured value of 2.17, with the swelling of the vitrinite group exceeding that of the whole coal. Thus, the results obtained from the piston apparatus may be distorted by differences in the packing of differently shaped maceral particles or as a result of the effects on the solvent activity by the extractable phase as discussed by Nishioka.³²

Pyridine extraction of coals and maceral concentrates usually increases the swelling ratio. The removal of the extractable molecular phase during pyridine extraction

close to its boiling point occurs as a result of the expansion of the coal structure due to swelling, cleavage of hydrogen bonding holding extractable material to the macromolecular structure, and thermal dissociation of other interactions. The diffusion exponents for the extracted coals and macerals indicate that solvent penetration is controlled by a case II diffusion mechanism. The removal of the extractable molecular phase therefore increases the rate at which swelling occurs. In addition, it may be assumed that the extractable phase does not swell appreciably under the experimental conditions used; hence, solvent extraction should increase swelling. However, in some cases small decreases in solvent swelling have been observed for the extracted coals compared with the raw coals. However, there is always the possibility that the solvent extraction causes some decomposition of the coal macromolecular structure. In addition, differences in the packing densities of raw and extracted coals may lead to differences.

Barton *et al.*⁴⁰ suggested that pyridine increases the mobility of parts of the macromolecular structure. On pyridine removal new coal-coal interactions could then be created as a result of the enhanced mobility of parts of the network during extraction. Larsen *et al.*⁵ have noted that native (raw) coal has few hydrogen bonds of strengths lower than about 21 kJ mol^{-1} . Pyridine extraction causes almost all of the coal-coal hydrogen bonds to break; on pyridine removal some new coal-coal bonds form, giving a greater range of bond strengths. They suggested that the most probable cause of the lack of lower strength hydrogen bonding in coal is the selective loss of hydroxyl groups during coalification, although it was also suggested that the most energetically favorable hydrogen bonds build up with time due to mobility of the network.

The calculated swelling ratio for extracted coal D based on the swelling of maceral group concentrates and its maceral composition is 1.52, compared to an experimental value of 1.58. The calculated ratio for coal K is 1.44, the same as that determined experimentally. There was insufficient material for a swelling ratio measurement to be carried out on the inertinite concentrate S for a similar calculation to be carried out for coal S. However, assuming that the coal follows the rule of addition, the swelling ratio of the inertinite should be about 1.26. This agrees with the lower swelling ratios for inertinite obtained with the other coals.

Inertinites are believed to be formed from the remains of charred plant material and would be expected to have a completely different structure from that of vitrinite. Inertinites have a high degree of aromaticity early on in the coalification pathway²⁰ and may have a higher covalent cross-link density. The effect on swelling may be similar to that found for coals of higher rank, for which the swelling ratio decreases abruptly above about 86% C.^{1,22} Maceral effects are secondary compared to the effect of rank; nevertheless, it has been shown that they could be important, particularly where inertinite contents are high, and the maceral composition of coals used in future solvent swelling studies should be quoted. An increase in the aromatic content and a decrease in the total oxygen content occurs with rank, with the remaining oxygen in high-rank coals being present in

(37) Nishioka, M.; Gebhard, L. A.; Silbernagel, B. G. *Fuel* **1991**, 70, 341.

(38) Tyler, R. J.; Schafer, N. S. *Fuel* **1980**, 59, 487.

(39) Hall, P. J. Ph.D. Thesis, University of Newcastle upon Tyne, 1987.

(40) Barton, A. B.; Lynch, L. J.; Webster, D. S. *Fuel* **1984**, 63, 1262.

heterocyclic configurations.⁴¹ Heteroatoms are important in charge transfer interactions between aromatic π - π systems,¹⁵ and these may remain undisrupted in the presence of basic solvents.

The PSD of extracted samples showed that agglomeration has taken place during the extraction procedure with a shift in the distribution to higher particle sizes. This suggests the possible presence of interparticle attractions holding the agglomerations together. The agglomerates were not broken down in the sonic bath in the presence of a surfactant. However, in pyridine the PSD shows no evidence of agglomerates. It is believed that the agglomerates are broken down in pyridine due to disruption of the interparticle bonding and by the increase in volume of the agglomerated particles as they swell. The result leads to the conclusion that PSDs are unsuitable for determining swelling ratios of coals extracted after micronization unless a procedure can be devised to overcome the agglomeration problem, possibly by passing the extracted coal through a fluid energy mill before measurement.

Conclusions

Equilibrium swelling increases in the order vitrinite > liptinite > inertinite for the extracted coals; however, for the raw coals the swelling of liptinite and vitrinite are almost equal for two of the three coals studied.

Extracted coals and maceral concentrates were found to have greater swelling ratios than raw samples. Diffusion exponents indicate that the swelling of raw coals and maceral concentrates solvent uptake are either anomalous or Fickian. After extraction, case II diffusion is indicated and the mechanism of solvent penetration is dependent on the relaxation of the macromolecular network. The low swelling ratios for inertinites suggest higher apparent covalent cross-link densities.

Comparison of the piston and PSD methods of obtaining Q_v shows that the use of particle size distributions avoids errors due to changing particle packing densities and gives an improved measure of real volumetric swelling. However, there is the possibility that for samples with a varying maceral composition with particle size, a skewed plot of swollen versus unswollen particle volume can be obtained as a direct result of the different swelling ratios of the maceral components. The demineralization process may modify the interactions within the coal structure; thus, swelling ratios obtained on demineralized samples should be viewed in this context. Interparticle interactions occur for the extracted micronized coal particles dispersed in water, resulting in particle agglomeration which makes the PSD methods unsuitable in these circumstances unless the problem of agglomeration can be overcome.

(41) Derbyshire, F. *Fuel* **1991**, 70, 277.