# Densities, porosities and surface areas of coal macerals as measured by their interaction with gases, vapours and liquids

Philip L. Walker, Jr., Shyam K. Verma*, Jose Rivera-Utrillat and Alan Davis

*Department of Materials Science and Engineering, and Energy and Fuels Research Center, The Pennsylvania State University, University Park, PA 16802, USA*
*(Received 29 February 1988; revised 18 April 1988)*

Helium, Hg, methanol, water and $CO_2$ were used as probes at 298 K to characterize densities, porosities and surface areas of coal macerals. Densities, measured by He and Hg displacement, permit the determination of maximum open pore volumes in macerals in the absence of significant imbibing of the fluids within the coal structure. Densities measured in methanol, water and $CO_2$ are frequently greater than those measured in He both because of their penetration into pores closed to He and into the coal structure due to imbibing. Imbibing into the coal structure results in the swelling of macerals, the extent of which is strongly rank dependent. Uptake of $CO_2$ on macerals is large. It is concluded that it is due primarily to pore filling (coverage of micropores) and not to penetration within the coal structure. Coverage of micropores by water is only a fraction of that found for $CO_2$. From this it is concluded that only a fraction of the surface of coal macerals is composed of hydrophilic sites.

(Keywords: macerals in coal; density; coal structure)

Interaction of various gases, vapours and liquids with coal continues to be of interest to the coal scientist and engineer. On the one hand, measurement of such interaction or uptake helps in our understanding of the chemical and physical structure of coal. On the other hand, information on such interaction enables the engineer to better understand such diverse processes as coal liquefaction and coal transport in slurry form. Interaction of fluids with coal is made both fascinating and complicated because coal is a microporous polymeric material containing significant numbers of heteroatoms in the form of diverse chemical functional groups. Its microporosity leads to the entrance of fluids into this porosity via the process of activated diffusion[1]. Coals behave as molecular sieve materials. Their polymeric nature, accompanied by the presence of diverse functional groups, leads to more or less chemical interactions of fluids with the solid through hydrogen bonding and/or electron transfer. Such interactions can prompt the building blocks in coal to move apart, allowing the fluid to enter, resulting in swelling[2]. Such change in structure has profound implications on the behaviour of coal as to its rate of liquefaction and its pumpability in slurry form.

This paper considers the interaction of a large number of coal macerals of varying rank with He, Hg, methanol, water and $CO_2$. From measurements of uptake of these various fluids on macerals, densities, porosities and surface areas are determined. Extents of swelling of macerals in methanol and water are also estimated.

---

Present addresses: * Calgon Carbon Co., Pittsburgh, PA 15230, USA
† University of Granada, Granada, Spain

## EXPERIMENTAL

### Maceral samples

In this study, hand-picked macerals of varying rank were used. The source of the macerals is given in *Table 1*. Measurements were made on −20 mesh material which had been stored under $N_2$ or Ar. Results for vitrinitic macerals in this paper pertain only to telocollinite, the predominant vitrinite sub-maceral in coal. In addition to the 39 vitrinite concentrates (>96%), two concentrates of resinite, one of fusinite and one of semifusinite were also obtained by hand picking. *Table 2* gives the analyses of the macerals. Procedures used for determining mineral matter and, hence, dmmf values are described elsewhere[3]. The rank assigned to the maceral concentrates was that of the whole coal from which they were taken.

### Surface area measurements

*From carbon dioxide sorption*. A volumetric apparatus was used to measure sorption of $CO_2$ at 298 K. A description of the procedure and apparatus is given elsewhere[4]. Prior to sorption, each sample was outgassed at 378 K under pressure less than $10^{-4}$ Pa for at least 15 h. A time of 30 min was allowed for each sorption point. This time was sufficient for the attainment of equilibrium for most coals. The Polanyi–Dubinin (P–D) equation[4] was used to convert sorption data to specific surface areas, with the molecular area of $CO_2$ taken as 0.253 $nm^2$ (Ref. 5). It has previously been shown that surface areas of coals calculated using the P–D equation are in good agreement with those calculated using the BET equation[6]. The P–D equation is used for sorption of $CO_2$

**Table 1** Source of macerals

| Sample PSMC | Seam | State | County |
|---|---|---|---|
| 15 | Lower Kittanning | PA | Jefferson |
| 17 | Lower Kittanning | PA | Jefferson |
| 19 | Lower Kittanning | PA | Armstrong |
| 21 | Lower Kittanning | PA | Clearfield |
| 22 | Lower Kittanning | PA | Clearfield |
| 23 | Lower Kittanning | PA | Jefferson |
| 25 | Lower Kittanning | PA | Venango |
| 26 | Lower Kittanning | PA | Lawrence |
| 27 | Lower Kittanning | PA | Lawrence |
| 28 | Lower Kittanning | PA | Clarion |
| 34 | Lower Kittanning | PA | Butler |
| 35 | Lower Kittanning | PA | Clarion |
| 42 | Lower Kittanning | PA | Clearfield |
| 43 | Lower Kittanning | PA | Indiana |
| 44 | Lower Kittanning | PA | Cambria |
| 46 | Lower Kittanning | PA | Cambria |
| 51 | Lower Kittanning | PA | Indiana |
| 53 | Lower Kittanning | PA | Somerset |
| 62 | Lower Kittanning | OH | Mahoning |
| 63 | Lower Kittanning (Ohio No. 5) | OH | Holmes |
| 64 | Lower Kittanning (Ohio No. 5) | OH | Tuscarawas |
| 65 | Lower Kittanning (Ohio No. 5) | OH | Perry |
| 66 | Lower Kittanning (Ohio No. 5) | OH | Jackson |
| 67 | Lower Kittanning (Ohio No. 5) | OH | Coshocton |
| 68 | Lower Kittanning (Ohio No. 5) | OH | Armstrong |
| 69 | Lower Kittanning (Ohio No. 5) | OH | Clearfield |
| 71 | Lower Kittanning (Ohio No. 5) | OH | Elk |
| 73 | Illinois No. 6 | IL | Knox |
| 74 | Illinois No. 6 | IL | Peoria |
| 76 | Illinois No. 6 | IL | Christian |
| 77 | Illinois No. 6 | IL | Vermillion |
| 78 | Illinois No. 7 | IL | Vermillion |
| 104 | Illinois No. 6 | IL | Montgomery |
| 105 | Illinois No. 6 | IL | St. Clair |
| 106 | Illinois No. 6 | IL | Randolph |
| 107 | Illinois No. 6 | IL | Jefferson |
| 108 | Illinois No. 6 | IL | Jackson |
| 109 | Illinois No. 6 | IL | Saline |
| 110 | Yallourn | Aust. | Victoria |
| 111 | Wyodak-Anderson | WY | Campbell |
| 112 | Bevier-Wheeler | MO | Howard |
| 114 | Wyodak-Canyon | WY | Campbell |
| 115 | Wyodak–Ft. Williams Formation | WY | Campbell |

**Table 2** Analysis of macerals

| Sample PSMC | VM wt%, dmmf | Chemical analysis (wt%, dmmf) | | | |
|---|---|---|---|---|---|
| | | C | H | O | $S_{org}$ |
| lvb | | | | | |
| 51 | 21.1 | 90.76 | 4.78 | 2.20 | 0.80 |
| mvb | | | | | |
| 42 | 27.7 | 89.76 | 5.38 | 2.95 | 0.88 |
| 44 | 24.3 | 89.92 | 5.24 | 3.43 | 0.66 |
| 53 | 18.7 | 89.55 | 4.67 | 3.90 | -- |
| hvAb | | | | | |
| 15 | 33.6 | 86.44 | 5.58 | 6.20 | -- |
| 17 | 38.2 | 85.10 | 5.53 | 6.92 | -- |
| 19 | 41.5 | 84.81 | 6.02 | 6.81 | -- |
| 21 | 27.5 | 88.63 | 5.39 | 3.75 | -- |
| 22 | 29.5 | 87.14 | 5.48 | 5.47 | -- |
| 23 | 32.3 | 86.31 | 5.62 | 6.31 | -- |
| 25 | 36.4 | 85.53 | 5.17 | 7.26 | 0.93 |
| 26 | 35.8 | 84.29 | 5.18 | 8.16 | 0.63 |
| 27 | 37.3 | 84.21 | 5.34 | 8.24 | 0.71 |
| 28 | 39.7 | 82.70 | 5.28 | 9.72 | 0.86 |
| 34 | 35.1 | 84.13 | 5.24 | 8.53 | 0.81 |
| 35 | 41.3 | 84.48 | 5.70 | 7.15 | 1.34 |
| 43 | 34.7 | 87.21 | 5.66 | 4.89 | 0.93 |
| 46 | 30.0 | 88.57 | 5.33 | 4.18 | 0.78 |
| 62 | 36.7 | 84.36 | 5.44 | 7.88 | -- |
| 63 | 41.2 | 83.10 | 5.25 | 9.27 | 1.36 |
| 64 | 42.5 | 82.60 | 5.54 | 9.25 | 1.93 |
| 65 | 38.2 | 81.77 | 5.28 | 10.75 | 0.65 |
| 67 | 41.8 | 82.74 | 5.54 | 9.50 | -- |
| 68 | 38.5 | 86.50 | 5.49 | 5.66 | 1.24 |
| 69 | 29.2 | 85.18 | 5.25 | 7.72 | 0.75 |
| 71 | 33.8 | 85.38 | 5.59 | 7.10 | -- |
| 77 | 41.6 | 81.91 | 5.61 | 9.71 | 1.95 |
| 78 | 40.0 | 81.76 | 5.46 | 10.22 | 1.56 |
| 104 | 42.1 | 81.77 | 5.14 | 10.07 | 2.49 |
| 105 | 42.9 | 82.47 | 5.20 | 9.61 | 2.43 |
| 106 | 41.4 | 82.68 | 5.13 | 9.54 | 1.97 |
| 107 | 36.6 | 83.04 | 5.16 | 8.81 | 0.67 |
| 108 | 34.3 | 84.22 | 4.90 | 7.70 | 0.57 |
| 109 | 34.9 | 83.68 | 5.29 | 8.36 | 1.62 |
| 119 | -- | 80.84 | 5.24 | 11.74 | 1.95 |
| hvBb | | | | | |
| 66 | 38.0 | 79.84 | 5.26 | 12.60 | 0.85 |
| 73 | 42.3 | 79.00 | 5.43 | 13.24 | 1.89 |
| 74 | 39.1 | 78.97 | 5.02 | 13.95 | 1.51 |
| 76 | 42.1 | 80.13 | 5.34 | 11.45 | 2.42 |
| 112[a] | -- | 92.54 | 3.82 | 3.00 | 1.06 |
| sub | | | | | |
| 111[b] | -- | 81.10 | 10.18 | 8.34 | 0.40 |
| 114[c] | -- | 81.17 | 3.63 | 14.94 | 0.36 |
| lig | | | | | |
| 110[b] | -- | 82.18 | 9.44 | 8.63 | -- |
| 115 | -- | 71.85 | 4.58 | 22.74 | 0.51 |

[a] 77% fusinite maceral
[b] 100% resinite maceral
[c] 80% semifusinite maceral

at 298 K, since it permits the use of uptake data measured below atmospheric pressure, despite the fact that the vapour pressure of $CO_2$ is 6.4 MPa.

*From water sorption.* A gravimetric apparatus was used to measure sorption of water at 298 K. A description of the procedure and apparatus is given elsewhere[+]. Outgassing conditions prior to a sorption run were the same as that used for $CO_2$ sorption. The attainment of equilibrium during water sorption required a much longer time than that required for $CO_2$ sorption. In most cases 4 h was sufficient; for some coals a longer time was required. The BET equation was used to convert sorption data to specific surface areas, with the molecular area of water taken as 0.106 $nm^2$ (Ref. 7). All surface areas could be duplicated within 5%.

*Density measurements*

*From Hg displacement.* As discussed elsewhere[+], Hg displacement can be used to determine the density of coal particles. Particle density is the weight of a unit volume of solid including pores and cracks. As described[+], a known weight of coal particles is placed in a penetrometer of known volume, which in turn is held in a porosimeter. In

order to obtain a meaningful particle density ($\rho_{Hg}$) of coal particles, it is essential to determine the minimum pressure which needs to be applied to the Hg in order to fill the interparticle void volume. In this study, a pressure of ≈0.41 MPa was required to fill the interparticle void volume between −20 mesh particles. From the Washburn equation[8], it is calculated that this pressure is sufficient to force Hg into voids as small as 3500 nm. Therefore, Hg is displaced by the volume of the solid and the volume of voids within the particles <3500 nm in diameter. The precision of Hg density measurements is approximately ±0.003 g $cm^{-3}$.

Table 3 Surface areas of macerals

| Sample PSMC | Surface area, m² g⁻¹ (dmmf) | | |
|---|---|---|---|
| | CO₂ (DP) | Water (BET) | Fraction of total area covered by water |
| lvb | | | |
| 51 | 240 | -- | — |
| mvb | | | |
| 42 | 189 | 8 | 0.04 |
| 44 | 202 | 16 | 0.08 |
| 53 | 256 | 26 | 0.10 |
| hvAb | | | |
| 15 | 167 | 34 | 0.21 |
| 17 | 184 | 43 | 0.23 |
| 19 | 168 | 30 | 0.18 |
| 21 | 209 | 22 | 0.10 |
| 22 | 120 | 22 | 0.18 |
| 23 | 131 | 31 | 0.24 |
| 25 | 291 | 58 | 0.20 |
| 26 | 220 | 40 | 0.18 |
| 27 | 248 | 50 | 0.20 |
| 28 | 172 | 54 | 0.31 |
| 34 | 199 | 42 | 0.21 |
| 35 | 128 | 28 | 0.22 |
| 43 | 173 | 15 | 0.09 |
| 46 | 186 | - | — |
| 47 | 228 | | |
| 62 | -- | 75 | |
| 63 | 266 | 113 | 0.43 |
| 64 | 189 | 110 | 0.58 |
| 65 | 264 | 98 | 0.37 |
| 67 | 261 | 76 | 0.29 |
| 68 | -- | 33 | - |
| 69 | 179 | 26 | 0.15 |
| 71 | 171 | 59 | 0.34 |
| 77 | 167 | 75 | 0.45 |
| 78 | 170 | 116 | 0.68 |
| 104 | 196 | 54 | 0.28 |
| 105 | 224 | 43 | 0.19 |
| 106 | 307 | 39 | 0.13 |
| 107 | 234 | 24 | 0.10 |
| 108 | 234 | 39 | 0.17 |
| 109 | – | 38 | |
| 113 | 201 | 42 | 0.21 |
| hvBb | | | |
| 66 | 278 | 102 | 0.37 |
| 73 | 195 | 121 | 0.62 |
| 74 | 210 | 71 | 0.34 |
| 76 | 200 | 106 | 0.53 |
| 112 | 135 | 26 | 0.19 |
| sub | | | |
| 111 | 62 | 4.7 | 0.08 |
| 114 | 314 | 168 | 0.54 |
| lig | | | |
| 110 | 63 | 0.54 | 0.01 |
| 115 | 303 | 221 | 0.73 |

As will be seen later, it was necessary to determine the macropore volume ($V_m$) of the coals and macerals. The International Union of Pure and Applied Chemistry defines macropores as those larger than 50 nm in diameter. Following determination of Hg densities at a pressure of ≈ 0.41 MPa, the pressure of the Hg was increased to 28.8 MPa to force Hg into voids down to a size of 50 nm. The volume of Hg forced into the particles between a pressure of 0.41 and 28.8 MPa is the macropore volume.

*From He displacement.* Since He is the smallest atom and is sorbed and imbibed by solids to a negligible extent at 298 K, it is widely used to measure densities of coals.

Procedures and apparatus used to measure He displacement (densities) have been fully described[4]. An equilibrium time of 30 min was generally sufficient. The precision of He density measurements is about ± 0.002 g cm⁻³.

*From liquid displacement.* Densities were determined from the displacement of methanol and water at 298 K, using the pycnometric method as described elsewhere[2,4]. Because water wets many coals poorly, a mixture of 1 wt % wetting agent (Triton X-100) in 99 wt % water was used. Since these liquids are imbibed by coals to some extent, depending upon rank, approach to equilibrium is slow[2]. For most coals and macerals, equilibrium was essentially reached within 24 h in the case of water uptake and about 70 h in the case of methanol uptake. Densities were reproducible to ± 0.003 g cm⁻³.

Densities measured by fluid displacement are on a dry mineral matter containing basis. Densities were corrected to a dry mineral matter free (dmmf) basis, taking the density of the mineral matter as 2.7 g cm⁻³ (Ref. 9).

## RESULTS

### Surface areas

Surface areas of −20 mesh macerals are presented in *Table 3*. Areas have been expressed on a dmmf basis, assuming that the amount of sorbate taken up as a monolayer on the mineral matter surface is negligible compared with that taken up as a monolayer on the organic matter surface[10].

### Densities and pore volumes

Densities ($\rho$) and pore volumes, as measured in different fluids, are presented in *Table 4* on a dmmf basis. Specific pore volumes, $V_f$, as measured by the displacement of He, water and methanol, are calculated from

$$V_f = \frac{1}{\rho_{He}} - \frac{1}{\rho_f} \tag{1}$$

when $\rho_f$ is the density measured in the appropriate fluid. The pore volume in $CO_2$ is calculated from the intercept on the axis of volume of $CO_2$ sorbed for the P–D plot at $[\log(P/P_0)]^2$ equal to zero[11]. The density of liquid sorbed $CO_2$ was taken as 1.037 g cm⁻³ (Dubinin, M. M., private communication).

### Swelling of coal macerals

When a fluid diffuses into the coal matrix, as distinct from the pore system, the result is swelling of the particles. This laboratory developed an approach recently to determine the amount of this swelling[2]. Swelling expressed in per cent, based on the specific volume of the coal maceral prior to exposure to a fluid, can be calculated as follows:

$$S = 100 \times \rho_{He}[(W_l/\rho_l) - V_f + V_m] \tag{2}$$

where $W_l$ is fluid uptake measured gravimetrically at a relative pressure of 0.95 and $\rho_l$ is density of the fluid, that is 0.7866 and 0.9971 g cm⁻³ for methanol and water (containing 1 % wetting agent) at 298 K. In turn, $V_l$ equals $W_l/\rho_l$. Swelling of macerals in methanol and water are presented in *Tables 5* and *6* along with values for $V_l$ and $V_m$. Values for $V_f$ and $\rho_{He}$ have been given previously. All values are reported on a dmmf basis.

**Table 4** Densities and pore volumes of macerals

| Sample PSMC | Densities (g cm$^{-3}$, dmmf) | | | | $V$, pore volume (cm$^3$ g$^{-1}$, dmmf) | | | | Open porosity (%) |
|---|---|---|---|---|---|---|---|---|---|
| | $\rho_{Hg}$ | $\rho_{He}$ | $\rho_{CH_3OH}$ | $\rho_{H_2O}$ | He | CH$_3$OH | H$_2$O | CO$_2$ | |
| **ivb** | | | | | | | | | |
| 51 | 1.220 | – | 1.342 | – | – | 0.0744 | – | 0.0611 | – |
| **mvb** | | | | | | | | | |
| 42 | 1.234 | 1.317 | 1.319 | 1.280 | 0.0516 | 0.0527 | 0.0297 | 0.0481 | 6.3 |
| 44 | 1.250 | 1.339 | 1.333 | 1.295 | 0.0531 | 0.0497 | 0.0278 | 0.0515 | 6.6 |
| 53 | 1.272 | 1.346 | 1.364 | 1.335 | 0.0432 | 0.0530 | 0.0371 | 0.0654 | 5.5 |
| **hvAb** | | | | | | | | | |
| 15 | 1.244 | 1.318 | 1.351 | 1.301 | 0.0450 | 0.0636 | 0.0351 | 0.0426 | 5.6 |
| 17 | 1.265 | 1.341 | 1.349 | 1.310 | 0.0448 | 0.0492 | 0.0271 | 0.0969 | 5.6 |
| 19 | 1.240 | 1.293 | 1.337 | 1.288 | 0.0329 | 0.0584 | 0.0299 | 0.0429 | 4.0 |
| 21 | 1.227 | 1.391 | 1.326 | 1.276 | 0.0960 | 0.0607 | 0.0312 | 0.0534 | 11.8 |
| 22 | 1.245 | 1.328 | 1.332 | 1.280 | 0.0501 | 0.0524 | 0.0219 | 0.0305 | 6.3 |
| 23 | 1.264 | 1.294 | 1.346 | 1.302 | 0.0183 | 0.0481 | 0.0230 | 0.0334 | 2.3 |
| 25 | 1.249 | 1.335 | 1.412 | 1.362 | 0.0516 | 0.0924 | 0.0664 | 0.0741 | 6.5 |
| 26 | 1.260 | 1.353 | 1.378 | 1.315 | 0.0545 | 0.0679 | 0.0332 | 0.0561 | 6.9 |
| 27 | 1.277 | 1.301 | 1.395 | 1.327 | 0.0144 | 0.0662 | 0.0295 | 0.0632 | 1.8 |
| 28 | 1.245 | 1.304 | 1.351 | 1.291 | 0.0363 | 0.0630 | 0.0286 | 0.0439 | 4.5 |
| 34 | 1.272 | 1.318 | 1.376 | 1.324 | 0.0274 | 0.0594 | 0.0309 | 0.0508 | 3.5 |
| 35 | 1.253 | 1.306 | 1.334 | 1.288 | 0.0323 | 0.0484 | 0.0216 | 0.0327 | 4.0 |
| 43 | 1.231 | 1.299 | 1.322 | 1.287 | 0.0424 | 0.0558 | 0.0352 | 0.0489 | 5.2 |
| 46 | 1.236 | 1.317 | 1.334 | 1.285 | 0.0497 | 0.0593 | 0.0308 | 0.0473 | 6.2 |
| 47 | 1.276 | – | 1.351 | – | – | 0.0435 | – | 0.0581 | – |
| **hvAb** | | | | | | | | | |
| 62 | 1.258 | 1.352 | 1.404 | 1.299 | 0.0553 | 0.0827 | 0.0251 | 0.0748 | 7.0 |
| 63 | 1.231 | 1.332 | 1.437 | 1.353 | 0.0616 | 0.1165 | 0.0738 | – | 7.6 |
| 64 | 1.224 | 1.298 | 1.400 | 1.327 | 0.0465 | 0.1026 | 0.0633 | 0.0483 | 5.6 |
| 65 | 1.214 | 1.339 | 1.482 | 1.361 | 0.0774 | 0.1491 | 0.0895 | 0.0672 | 9.4 |
| 67 | 1.241 | 1.288 | 1.406 | 1.324 | 0.0293 | 0.0945 | 0.0504 | 0.0666 | 3.6 |
| 68 | 1.230 | 1.270 | 1.316 | 1.261 | 0.0255 | 0.0530 | 0.0199 | – | 3.1 |
| 69 | 1.237 | 1.306 | 1.335 | 1.292 | 0.0426 | 0.0592 | 0.0343 | 0.0457 | 5.3 |
| 71 | 1.244 | 1.310 | 1.339 | 1.325 | 0.0404 | 0.0570 | 0.0491 | 0.0436 | 5.0 |
| 77 | 1.045 | 1.311 | 1.410 | 1.325 | 0.1943 | 0.2479 | 0.2024 | 0.0426 | 20.4 |
| 78 | 1.075 | 1.417 | 1.428 | 1.408 | 0.2242 | 0.2297 | 0.2197 | 0.0435 | 24.2 |
| 104 | 1.066 | 1.324 | 1.412 | 1.336 | 0.1829 | 0.2300 | 0.1897 | 0.0500 | 19.6 |
| 105 | 1.127 | 1.313 | 1.386 | 1.315 | 0.1254 | 0.1655 | 0.1266 | 0.0570 | 14.2 |
| 106 | 1.191 | 1.301 | 1.417 | 1.329 | 0.0708 | 0.1337 | 0.0870 | 0.0783 | 8.4 |
| 107 | 1.147 | 1.320 | 1.436 | 1.331 | 0.1142 | 0.1754 | 0.1204 | 0.0597 | 13.1 |
| 108 | 1.167 | 1.332 | 1.430 | 1.339 | 0.1061 | 0.1575 | 0.1100 | 0.0596 | 12.4 |
| 109 | 1.202 | 1.291 | 1.395 | 1.306 | 0.0579 | 0.1156 | 0.0668 | – | 6.9 |
| 113 | 1.125 | 1.348 | 1.405 | 1.303 | 0.1467 | 0.1768 | 0.1211 | 0.0514 | 16.6 |
| **hvBb** | | | | | | | | | |
| 66 | 1.241 | 1.405 | 1.488 | 1.374 | 0.0940 | 0.1337 | 0.0779 | 0.0708 | 11.7 |
| 73 | 1.047 | 1.351 | 1.495 | 1.399 | 0.2150 | 0.2864 | 0.2405 | 0.0498 | 22.6 |
| 74 | 1.054 | 1.372 | 1.449 | 1.343 | 0.2197 | 0.2585 | 0.2040 | 0.0535 | 23.1 |
| 76 | 1.083 | 1.325 | 1.436 | 1.350 | 0.1681 | 0.2266 | 0.1821 | 0.0510 | 18.2 |
| 112 | 1.160 | 1.525 | 1.532 | 1.437 | 0.2067 | 0.2093 | 0.1667 | 0.0343 | 24.0 |
| **sub** | | | | | | | | | |
| 111 | 1.018 | 1.071 | 1.129 | 1.080 | 0.0494 | 0.0973 | 0.0572 | 0.0157 | 5.0 |
| 114 | 1.067 | 1.473 | 1.608 | 1.088 | 0.2582 | 0.3155 | 0.0178 | 0.0801 | 27.6 |
| **lig** | | | | | | | | | |
| 110 | 1.033 | 1.079 | 1.160 | 1.087 | 0.0415 | 0.1063 | 0.0483 | 0.0160 | 4.3 |
| 115 | 1.315 | 1.465 | 1.599 | 1.461 | 0.0780 | 0.1351 | 0.0761 | 0.0774 | 10.3 |

## DISCUSSION

It is to be emphasized that measurements of physical properties of a molecular sieve, heteropolymeric substance having acidic and basic functional groups on part of its surface, like coal, are affected by many variables. Therefore, there are no unique values for the physical properties for a coal. Coals contain voids (pores) of molecular dimensions that can be more or less blocked by monolayers of sorbed organic species and water. Thus, conditions used for sample preparation prior to a physical measurement (extent of grinding, outgassing temperature and time, and quality of vacuum used) can affect the extent to which fluids are removed from the pore system. Water which is held tightly on carboxyl groups in the acid or salt form in low rank coals is a particular problem. Values for the physical properties presented in this study should be considered in this light. Certainly, they should be considered when comparing them to measurements made by other workers who may have used somewhat different preparation procedures.

*Porosity in coal macerals*

As stated in the Introduction, cross-linking along with poor packing of irregular building blocks which exist in

**Table 5** Swelling of macerals in methanol

| Sample PSMC | $V_i$ (cm³ g⁻¹, dmmf) | $V_m$ (cm³ g⁻¹, dmmf) | Swelling (%) |
|---|---|---|---|
| lvb | | | |
| 51 | 0.0610 | 0.0259 | 1.53 |
| mvb | | | |
| 42 | 0.0570 | 0.0223 | 3.28 |
| 44 | 0.0433 | 0.0284 | 2.75 |
| 53 | 0.0626 | 0.0314 | 5.21 |
| hvAb | | | |
| 15 | 0.0529 | 0.0168 | 0.76 |
| 17 | 0.0856 | 0.0227 | 7.47 |
| 19 | 0.0721 | 0.0209 | 4.29 |
| 21 | 0.0545 | 0.0181 | 1.46 |
| 22 | 0.0520 | 0.0258 | 3.16 |
| 23 | 0.0547 | 0.0168 | 2.96 |
| 25 | 0.1398 | 0.0173 | 8.08 |
| 26 | 0.1117 | 0.0270 | 8.92 |
| 27 | 0.0880 | 0.0313 | 6.78 |
| 28 | 0.0790 | 0.0193 | 4.40 |
| 34 | 0.1068 | 0.0486 | 12.2 |
| 35 | 0.0560 | 0.0141 | 2.71 |
| 43 | 0.0495 | 0.0280 | 2.67 |
| 46 | 0.0527 | 0.0173 | 1.32 |
| 47 | 0.0715 | 0.0200 | 6.12 |
| 62 | 0.1640 | 0.0158 | 12.2 |
| 63 | 0.2972 | 0.0177 | 24.4 |
| 64 | 0.1957 | 0.0180 | 13.6 |
| 67 | 0.2768 | 0.0170 | 24.7 |
| 69 | 0.0662 | 0.0198 | 3.32 |
| 71 | 0.0740 | 0.0185 | 4.41 |
| 77 | 0.3681 | 0.0234 | 15.0 |
| 78 | 0.3658 | 0.0243 | 17.3 |
| 104 | 0.3420 | 0.0286 | 15.0 |
| 105 | 0.2954 | 0.0229 | 17.2 |
| 106 | 0.2977 | 0.0215 | 22.1 |
| 107 | 0.2311 | 0.0222 | 8.90 |
| 108 | 0.2277 | 0.0213 | 10.7 |
| 109 | 0.2064 | 0.0197 | 13.3 |
| 113 | 0.2469 | 0.0211 | 10.3 |
| hvBb | | | |
| 73 | 0.4451 | 0.0252 | 19.3 |
| 76 | 0.3088 | 0.0331 | 12.5 |
| sub | | | |
| 111 | 0.1134 | 0.0442 | 6.14 |
| 114 | 0.1837 | 0.2119 | 8.60 |
| lig | | | |
| 110 | 0.3171 | 0.0297 | 24.9 |
| 115 | 0.3118 | 0.0437 | 29.0 |

**Table 6** Swelling of macerals in water

| Sample PSMC | $V_i$ (cm³ g⁻¹, dmmf) | $V_m$ (cm³ g⁻¹, dmmf) | Swelling (%) |
|---|---|---|---|
| mvb | | | |
| 42 | 0.0223 | 0.0223 | 1.84 |
| 44 | 0.0245 | 0.0284 | 3.14 |
| 53 | 0.0337 | 0.0314 | 3.56 |
| hvAb | | | |
| 15 | 0.0356 | 0.0168 | 2.15 |
| 17 | 0.0416 | 0.0227 | 4.70 |
| 19 | 0.0434 | 0.0209 | 4.26 |
| 21 | 0.0236 | 0.0181 | 1.29 |
| 22 | 0.0209 | 0.0258 | 3.08 |
| 23 | 0.0317 | 0.0168 | 3.22 |
| 25 | 0.0687 | 0.0173 | 2.45 |
| 26 | 0.0536 | 0.0270 | 5.97 |
| 27 | 0.0579 | 0.0313 | 7.62 |
| 28 | 0.0385 | 0.0193 | 3.64 |
| 34 | 0.0445 | 0.0486 | 7.92 |
| 35 | 0.0388 | 0.0141 | 3.92 |
| 43 | 0.0286 | 0.0280 | 2.63 |
| 46 | 0.0233 | 0.0173 | 1.21 |
| 62 | 0.0716 | 0.0158 | 7.83 |
| 63 | 0.1242 | 0.0177 | 8.38 |
| 64 | 0.0827 | 0.0180 | 4.58 |
| 65 | 0.1215 | 0.0261 | 7.06 |
| 67 | 0.0745 | 0.0170 | 5.10 |
| 68 | 0.0256 | 0.0210 | 3.29 |
| 69 | 0.0234 | 0.0198 | 1.10 |
| 71 | 0.0456 | 0.0185 | 1.87 |
| 77 | 0.1939 | 0.0234 | 1.55 |
| 78 | 0.2149 | 0.0243 | 2.10 |
| 104 | 0.1742 | 0.0286 | 1.40 |
| 105 | 0.1467 | 0.0229 | 4.84 |
| 106 | 0.1311 | 0.0215 | 7.81 |
| 107 | 0.1373 | 0.0222 | 4.48 |
| 108 | 0.1279 | 0.0213 | 4.58 |
| 109 | 0.0961 | 0.0197 | 5.89 |
| 113 | 0.1127 | 0.0211 | 1.43 |
| hvBb | | | |
| 66 | 0.1457 | 0.0230 | 11.3 |
| 73 | 0.2693 | 0.0252 | 5.65 |
| 74 | 0.1882 | 0.0309 | 0.96 |
| 76 | 0.2229 | 0.0331 | 8.01 |
| 112 | 0.0456 | 0.1219 | 0.09 |
| sub | | | |
| 114 | 0.1260 | 0.2119 | 34.2 |
| lig | | | |
| 115 | 0.2224 | 0.0437 | 25.0 |

coal would be expected to result in porosity being present within the coal structure. The presence of porosity within a broad range of pore diameters including micropores (<2 nm), transitional pores (2–50 nm), and macropores (>50 nm) has been confirmed by electron microscopy[12,13] and small angle X-ray scattering (SAXS) studies[14–17]. It was the purpose of this study to characterize the porosity in coal by an independent technique, that is, by exposure of coal to various fluids at room temperature. Let us now consider what results obtained from this approach tell us about the nature of coal-fluid interaction and porosity in coal.

As we have seen in the results, when coals are exposed to some fluids, they swell and expand; thus their structure (and undoubtedly their porosity) has been altered. As useful as these results will be from both a practical and a fundamental viewpoint in aiding in our understanding of porosity in coal, results on reference coal-fluid systems are needed where coal structure is altered to a negligible

extent. Two fluids that are of particular use are Hg and He. Since Hg has a contact angle with the surface of coals of ≈ 140°, it only penetrates into the porosity of coal if an external pressure is applied—the higher the pressure, the smaller the pore size into which Hg is forced. Thus Hg is displaced by the combined volume of the solid structure of the coal and all pores below a certain size. In this study for the determination of Hg densities ($\rho_{Hg}$), that is weight of coal per unit volume of solid and pores, a pressure of 0.41 MPa was applied to the Hg. At this pressure, which will produce negligible contraction of the coal particles[2], pores <3500 nm in diameter will displace Hg.

The combination of He being an inert gas, the smallest molecule, and sorbing to a negligible extent in coal at room temperature[18] makes it an ideal molecule to use to probe the pore structure in coal. Exposure of coal to He at 298 K results in negligible volume change (swelling) of the coal, even at pressures as high as 3.4 MPa[19]. It is estimated that He can penetrate rapidly into pores
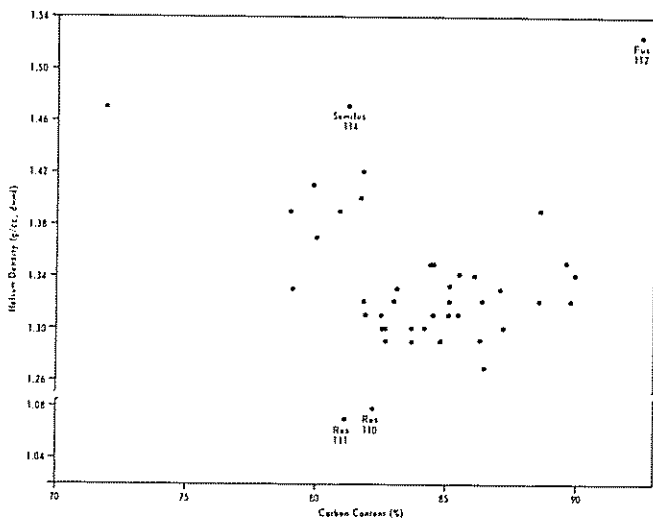
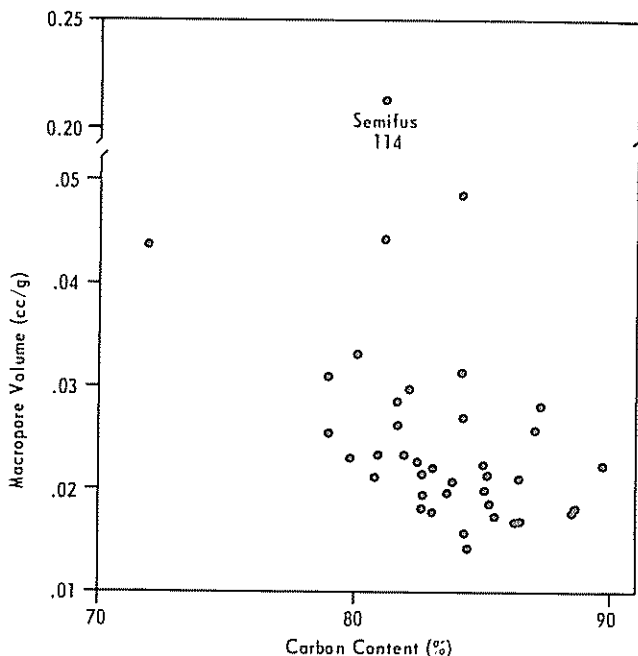**Figure 1** Helium density of macerals as a function of their carbon content



**Figure 2** Macropore volume of macerals as a function of their carbon content

$> \approx 0.42\,nm$ in diameter at room temperature[1]. Therefore, in the determination of He densities $(\rho_{He})$, He is displaced by the combined volume of the solid structure and all pores (or pores behind apertures) $< 0.42\,nm$ in diameter. Thus, the maximum, total open pore volume in coals, in $cm^3\,g^{-1}$, is given by

$$V_T = \frac{1}{\rho_{Hg}} - \frac{1}{\rho_{He}} \qquad (3)$$

It was reported earlier[9,18] that $\rho_{He}$ goes through a shallow minimum with increasing coal rank for coals high in vitrinite and then rises very sharply for anthracites of highest carbon content. The minimum has been attributed[18] to a change in the average number of aromatic and hydroaromatic rings in coal per carbon

atom present from $\approx 0.27$ in lignite, to a minimum of $\approx 0.24$ in coals of 83–84% carbon, followed by a sharp rise for the anthracites. The end member is graphite (100% carbon) with a ring to carbon atom ratio of 0.5. Despite this general trend of change in $\rho_{He}$ with coal rank, there is considerable variation in $\rho_{He}$ for vitrinitic coal macerals of given rank, as seen in *Table 4*.

*Figure 1* presents data for the $\rho_{He}$ of macerals as a function of their carbon content (rank). For vitrinitic macerals, there is a general decrease in $\rho_{He}$ with increasing carbon content from 72 to 90%. Macerals high in resinite (PSMC-110 and 111) have $\rho_{He}$ which fall considerably below those for vitrinites of equivalent carbon content; whereas macerals high in fusinite or semifusinite (PSMC-112 and 114) have $\rho_{He}$ which fall considerably above those for vitrinites.

Neavel *et al.*[20] previously measured $\rho_{He}$ on 66 coals of varying rank and $16 \times 100$ mesh particle size. Their expression, accounting for 94.3% of the variance of the densities of the samples, was

$$\rho_{He} = 0.023(C) + 0.0292(O) - 0.0261(H) + 0.0225(S_{org})$$
$$- 0.765 \qquad (4)$$

in which the elements are expressed as wt% on a dmmf basis. Equation (4) correlated our $\rho_{He}$ data on 32 macerals for which we had organic S data less well (namely $r^2 = 0.749$). Our best fit expression, Equation (5)

$$\rho_{He} = 0.033(C) + 0.036(O) - 0.031(H) + 0.009(S_{org})$$
$$- 1.577 \qquad (5)$$

accounted for 83.3% of the variance of the densities of the maceral samples.

The expression that best fits the $\rho_{He}$ data will depend upon the precise procedures used to measure these densities, as just discussed, and the particle size of the samples on which measurements were made. Coals contain some porosity which is effectively closed to He at room temperature[11]. The smaller the particle size of the coal on which measurements are made, the greater the extent to which closed pore volume is opened up and thus made accessible to He. This results in an increase in measured $\rho_{He}$. Helium densities calculated by Equation
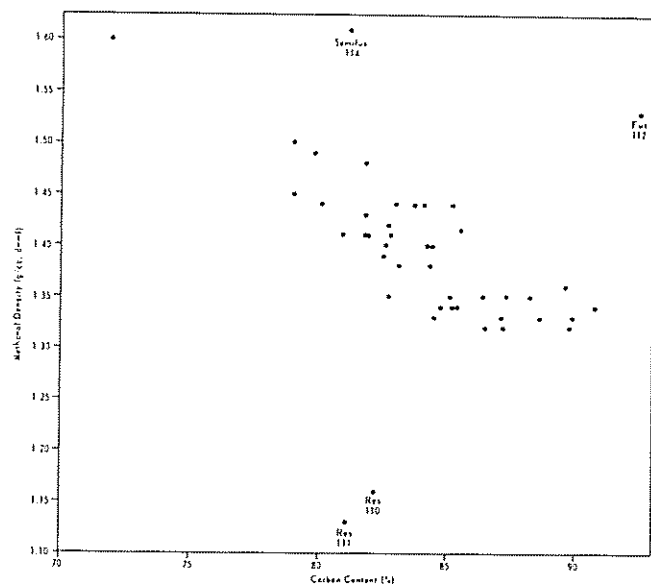


**Figure 3** Methanol densities of macerals as a function of their carbon content
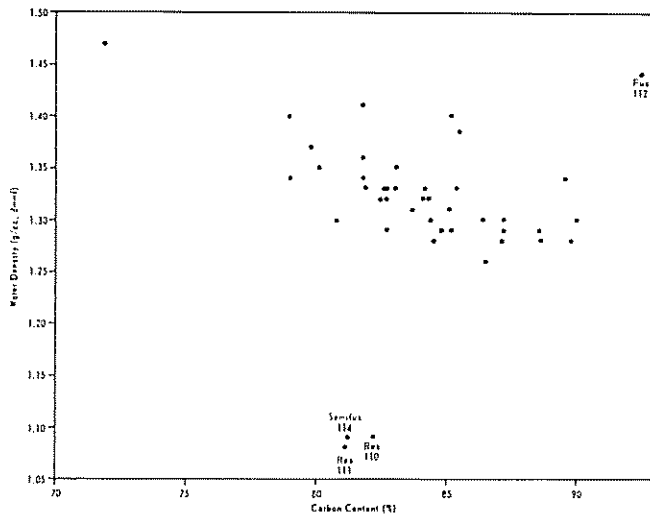
Figure 4 Water densities of macerals as a function of their carbon content

(4), given by Neavel *et al.*[20], were, on average, lower than those measured experimentally in this study. This is consistent with their using a somewhat larger particle size consist in their study.

It has been pointed out by Mahajan[21] that most coals high in vitrinite have $\rho_{Hg}$ values falling in the range 1.17 to 1.27 g cm$^{-3}$. As seen in *Table 4*, this is consistent with our findings for coal macerals. Unlike $\rho_{He}$, however, the correlation of $\rho_{Hg}$ with elemental analysis (C, H, O, S$_{org}$) was poor. The best fit expression only accounted for 41.5% of the variance of the densities of the maceral samples.

Even though there is some trend of increasing pore volume accessible to He with decreasing coal rank, large variations exist within coal macerals of the same rank. Porosities, that is the per cent of particle volume which is volume accessible to He, also show some trend to increase with decreasing coal rank; but much scatter in values within the same rank is seen. Porosities range from 1.8 to 27.6% for the macerals studied. Two of the largest values are those shown by the fusinite concentrates. In view of their open cellular structure, this is to be expected.

*Figure 2* summarizes results for the macropore volumes of macerals of varying rank. Some trend of increasing macropore volume with decreasing rank is seen. The semifusinite maceral (PSMC-114) is seen to have a very high macropore volume compared to vitrinitic macerals of all ranks.

*Swelling of coal macerals in different fluids*

Since He is the smallest molecule, if pore volumes reported to be accessible to other fluids are larger than those accessible to He, it is clear that their interaction with coal has altered the coal structure resulting, probably, in swelling. Higher pore volumes are seen to be the case, frequently but not always, when coals and macerals are exposed to methanol, water and $CO_2$ at 298 K. By using a combination of pyncometric and gravimetric approaches, the extent of coal swelling in the presence of liquid methanol and liquid water has been determined.

Pycnometric densities of macerals as measured in methanol and water are summarized as a function of rank

(carbon content) in *Figures 3* and *4*. For the vitrinites, there is a general increase in density with decreasing rank. Maceral concentrates of fusinite, semifusinite and resinite show densities which differ considerably from those for the vitrinites of equal carbon contents.

When a porous solid is exposed to a fluid, swelling can be produced by at least two phenomena: (i) adsorption of a liquid-like layer on the surface of the pores[22-25]; and (ii) imbibition or intercalation of the fluid into the solid structure itself[26]. In the first instance, if the solid has a high surface area (meaning an abundance of micropores), adsorption results in the creation of pressure gradients which are sufficiently large ($\approx 10^6$ g cm$^{-2}$) to cause measurable deformation of the solid[22]. In the second instance, chemical interaction of the fluid with the solid through hydrogen bonding and/or electron transfer can prompt the building blocks in the solid to move apart, allowing the fluid to enter. Swelling due to adsorption, even in solids of high surface area, is relatively small. Swelling due to imbibition can range from negligible to large, depending upon the extent of chemical or physical interaction of the fluid with the solid.

Let us consider some extreme examples of the results obtained when solids of different chemical and physical structures are exposed to fluids[2]. First, consider a macroporous, partially cross-linked polymer—a tripolymer of styrene (88%), divinyl benzene (4%) and ethylene glycol dimethacrylate (8%). The molecular weight between cross-links is estimated at 1240 (Ref. 2). The polymer contains a negligible volume of pores closed to He. For this polymer, $\rho_{He}$ is 1.075 g cm$^{-3}$ compared with $\rho_{methanol}$ and $\rho_{benzene}$, as measured pycnometrically, of 1.078 and 1.101 gcm$^{-3}$, respectively. The densities and accessible pore volumes are essentially the same, even though extensive swelling of the polymer occurred in the fluids—65.5% in benzene. In this case, the large volume of fluid which was imbibed into the polymer produced essentially an equal volume displacement of fluid. The result is a net volume displacement of fluid in the pyncometer equal to the original volume of the solid and
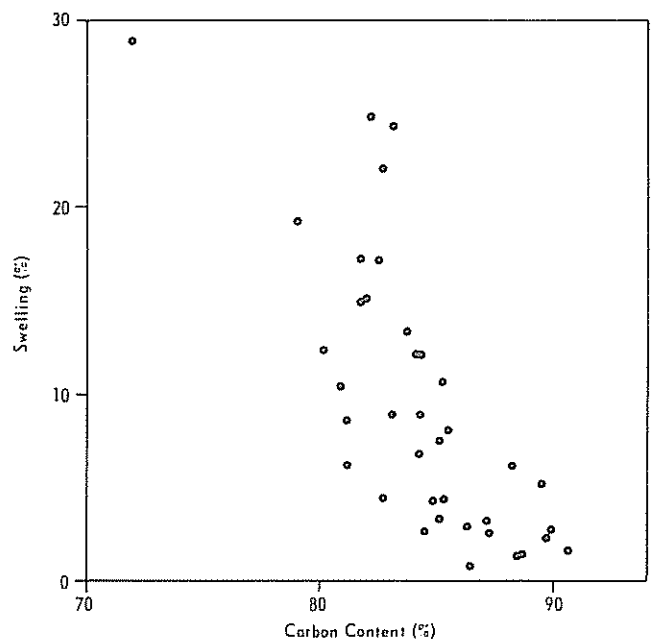


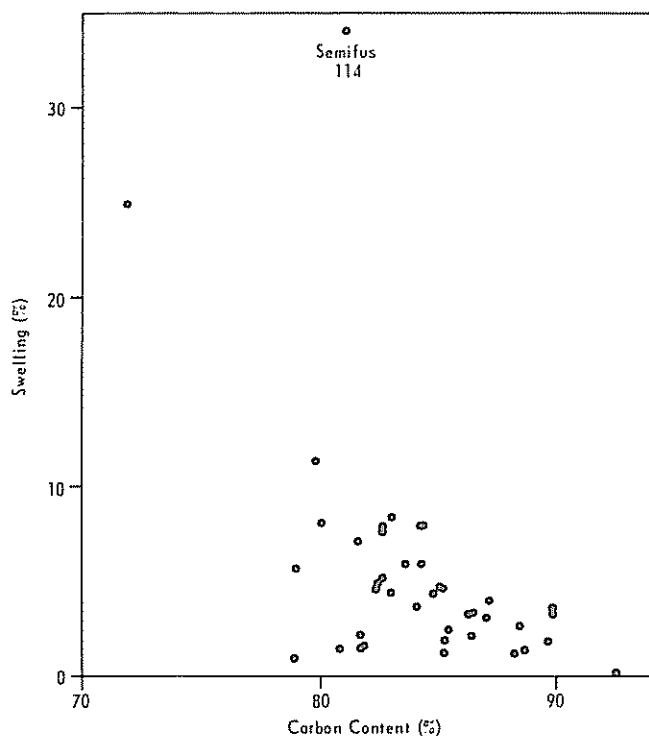Figure 5 Swelling of macerals in methanol as a function of their carbon content

**Figure 6** Swelling of macerals in water as a function of their carbon content

agreement of $\rho_{fluid}$ with $\rho_{He}$.

Second, consider a Saran char of high surface area[27], derived from the copolymer divinylidene chloride and divinyl chloride. It was prepared at 1173 K. Like all carbons containing small amounts of heteroatoms and well-formed trigonally bonded carbon crystallites, it will imbibe fluids to a negligible extent. In addition to a large microporosity, it will contain some porosity inaccessible to He. That is, the pores are irregular in size or of a cavity–aperture type, with some apertures $<0.42$ nm in diameter. For this material, the $\rho_{He}$ (2.049 g cm$^{-3}$) is greater than $\rho_{methanol}$ and $\rho_{benzene}$ values of 1.961 and 1.930 g cm$^{-3}$, respectively[2]. Fluid densities are lower than $\rho_{He}$ since imbibition, which would allow the fluid to permeate through the solid structure and also gain access to the closed pores, is negligible. Swelling of the Saran, due to adsorption of the fluid, is also not sufficient to permit fluid penetration into a pore volume greater than that which is accessible to He.

Now, we can consider coals, which exhibit a behaviour intermediate between the two cases just discussed. Coals combine the ability to imbibe some fluids, with the existence of pores closed to He. Like Saran char, the pores in coal are thought to contain numerous fine constrictions, some of which are not accessible to He[28]. If the amount of fluid imbibed is sufficient, the fluid will be able to bypass the constrictions (apertures) and gain access to significant volumes of pores (cavities) which were closed to He. The result will be fluid densities which exceed $\rho_{He}$, if the volume of fluid gaining access to the closed pores does not result in equal volume swelling of the coal. Unlike volume swelling being equal to volume uptake in the case of imbibition, volume swelling is expected to be considerably less than volume uptake in closed pores. Like us, Franklin[28] and Nelson et al.[2] have also reported $\rho_{methanol}$ to exceed $\rho_{He}$ for coals.

If the above reasoning is essentially correct, one can

estimate from data in *Table 4* the volume of pores closed to He but open to a particular fluid as ($V_{f,fluid} - V_{f,He}$). With few exceptions, $V_{f,methanol} > V_{f,He}$. In many cases ($V_{f,methanol} - V_{f,He}$) is a considerable fraction of $V_{f,He}$; in some cases it exceeds $V_{f,He}$. For water and $CO_2$ (at the low relative pressure of $CO_2$ used in this study), $V_{f,fluid}$ less frequently exceeds $V_{f,He}$.

The main cause of swelling of most coals and macerals in methanol and water is attributed to their hydrogen bonding with phenolic hydroxyl and carboxyl groups in the coals. Coals, ranging in carbon content from 91 to 76% show essentially a linear increase in phenolic hydroxyl content with decreasing carbon content[29]. For coals of lower rank, phenolic hydroxyl content remains essentially constant[30]; but carboxyl groups are now present, increasing in amount with decreasing rank. Therefore, it would be expected that swelling of coal macerals in methanol and water increases with decreasing rank (decreasing carbon content). Such is the case, as seen in *Figures 5* and *6*. It is noted, in *Figure 6*, that the maceral concentrate high in semifusinite (PSMC-114) swells to a much greater extent than vitrinites of equivalent carbon content. This is attributed to the combination of its having a higher oxygen content as well as an unusually large total pore volume.

*Surface areas of coal*

The interpretation of the surface areas of coals as measured by $CO_2$ uptake has recently been considered at some length[19]. Despite the fact that $CO_2$ uptake on coals frequently exceeds that of He uptake, we have shown, through dilatometric studies, that volume swelling of coals in $CO_2$ at pressures of $CO_2$ where surface area measurements are made is much smaller than measured uptake volume of $CO_2$. Thus, as discussed previously, most of the $CO_2$ taken up is not imbibing within the coal structure. Most $CO_2$ uptake at pressures at which surface areas are measured is going into open and closed pores (primarily micropores). Thus, as seen in *Table 3*, coal macerals have a large surface accessible to $CO_2$. Unlike $CO_2$, water only sorbs on hydrophilic surface sites[7], which in the case of coals would be predominantly those covered by oxygen functional groups—hydroxyl and carboxyl groups. Thus, despite the fact that the water molecule has a slightly smaller minimum kinetic diameter than does the $CO_2$ molecule (0.27 nm *versus* 3.3 nm), water coverage on maceral surfaces is less than $CO_2$ coverage. That is, only a fraction of coal maceral surfaces is covered by hydrophilic sites. Within a given rank of vitrinitic macerals (hvAb, for example), the fraction of the $CO_2$ surface area which is covered by water, varies widely, as is seen in *Table 3*. Generally, however, the fraction covered by water ranges from 0.15 to 0.25 for the vitrinitic macerals. The fractional coverage by water is particularly dependent upon maceral composition. Low rank coal macerals high in resinite (PSMC-110 and 111) or fusinite (PSMC-112) have much smaller fractions of their $CO_2$ areas covered by water than do vitrinitic macerals of equivalent rank. This clearly indicates that most of the surfaces in resinitic and fusinitic macerals are composed of hydrophobic sites.

ACKNOWLEDGEMENTS

## REFERENCES

1    Walker, P. L., Jr., Austin, L. G. and Nandi, S. P. in 'Chemistry and Physics of Carbon' (Ed. P. L. Walker, Jr.), Marcel Dekker, NY, 1966, Vol. 2, pp. 257–371
2    Nelson, J. R., Mahajan, O. P. and Walker, P. L., Jr. *Fuel* 1980, **59**, 831
3    Given, P. H. and Yarzab, R. F. in 'Analytical Methods for Coal and Coal Products' (Ed. C. Karr, Jr.), Academic Press, NY, 1978, Vol. 2, pp. 3–41
4    Mahajan, O. P. and Walker, P. L., Jr. in 'Analytical Methods for Coal and Coal Products' (Ed. C. Karr, Jr.), Academic Press, NY, 1978. Vol. 1, pp. 125–162
5    Walker, P. L., Jr. and Kini, K. A. *Fuel* 1965, **44**, 453
6    Walker, P. L., Jr. and Patel, R. L. *Fuel* 1970, **49**, 91
7    Walker, P. L., Jr. and Janov, J. J. *Colloid Interfac. Sci.* 1968, **28**, 449
8    Washburn, E. W. *Proc. Nat. Acad. Sci. U.S.* 1921, **7**, 115
9    Gan, H., Nandi, S. P. and Walker, P. L., Jr. *Fuel* 1972, **51**, 272
10   O'Gorman, J. V., Ph.D. Thesis, The Pennsylvania State University, 1971
11   Walker, P. L., Jr. *Phil. Trans. Roy. Soc. London* 1981, **A300**, 65
12   Waisman, B. A., Krivitzkii, M. D. and Krigman, F. E. *Dokl. Akad. Nauk. USSR* 1954, **97**, 1031
13   Harris, L. A. and Yust, C. S. *Fuel* 1976, **55**, 233
14   Spitzer, Z. and Ulicky, L. *Fuel* 1976, **55**, 212
15   Lin, J. S., Hendricks, R. W., Harrison, L. A. and Yust, C. S. *J. Appl. Cryst.* 1978, **11**, 621
16   Schmidt, P. W., Kwak, C. Y. and Kalliot, M. *Am. Chem. Soc., Div. Fuel Chem. Prepr.* 1983, **28** (4), 75
17   Setek, M., Snook, I. K. and Wagenfeld, H. K. *Am. Chem. Soc., Div. Fuel Chem. Prepr.* 1983, **28** (4), 81
18   van Krevelen, D. W. and Chermin, H. A. G. *Fuel* 1954, **33**, 79
19   Walker, P. L., Jr., Verma, S. K., Rivera-Utrilla, J. and Khan, M. R. *Fuel* 1988, **67**, 719
20   Neavel, R. C., Hippo, E. J., Smith, S. E. and Miller, R. N. *Am. Chem. Soc., Div. Fuel Chem. Prepr.* 1980, **25** (3), 246
21   Mahajan, O. P. in 'Coal Structure' (Ed. R. A. Meyers), Academic Press, NY, 1983, pp. 50–86
22   Bangham, D. H. and Maggs, F. A. P., Proc. Conf. Ultra-Fine Structures of Coals and Cokes, BCURA, 1944, p. 118
23   Flood, E. A. *Can. J. Chem.* 1957, **35**, 48
24   Flood, E. A. and Forhan, F. M. *Can. J. Chem.* 1963, **41**, 1703
25   Dacey, J. R. and Cadenhead, D. A., Proc. Fourth Carbon Conf., Pergamon Press, Oxford, 1960, p. 9
26   Flory, P. J. and Rehner, J., Jr. *J. Chem. Phys.* 1943, **11**, 521
27   Lamond, T. G., Metcalfe, J. E. and Walker, P. L., Jr. *Carbon* 1965, **3**, 59
28   Franklin, R. E. *Trans. Faraday Soc.* 1949, **45**, 274
29   Abdel-Baset, Z., Given, P. H. and Yarzab, R. F. *Fuel* 1978, **57**, 95
30   van Krevelen, D. W. and Schuyer, J. in 'Coal Science', Elsevier, Amsterdam, 1957, p. 218

# The mode of occurrence of chlorine in high volatile bituminous coals from the Asturian Central coalfield

## M. Rosa Martinez-Tarazona, José M. Palacios* and José M. Cardín

*Instituto Nacional del Carbón y sus Derivados (CSIC), La Corredoria 33011 Oviedo, Spain*
*\* Instituto de Química Física 'Rocasolano' (CSIC), Serrano 119, 28006 Madrid, Spain*
*(Received 26 February 1988; revised 26 April 1988)*

The occurrence of chlorine in two high volatile bituminous coals from the Asturian Central coalfield, with a chlorine content about 0.1 wt % has been discussed. The methodology used is based on obtaining the chlorine distribution in different densimetric fractions in gravimetric solutions free of chlorides. It allows the separation of elements that could be bonded to chlorine to study their likely association. Additional information has been obtained by carrying out studies on the solubility in water, and the relation of chlorine with alkaline and alkaline-earth elements. Direct evidence of the presence of chlorine and its chemical association has been gained by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). From the results it may be concluded that in the coals studied chlorine is mainly localized in the coal matrix associated to organic matter.

(Keywords: scanning electron microscopy; bituminous coal; density)

The presence of chlorine in coal causes corrosion and fouling problems in combustion and conversion processes. The severity depends not only on the chlorine content but on its chemical state. The chlorine concentration ranges from 0 wt% in some coals from Illinois basin[1] to about 1 wt % in certain samples from the UK[2]. The Asturian coals have an intermediate concentration, lower than 0.3 wt %[3] and experience has shown that serious problems may occur if this level is exceeded.

It is expected that in future the chlorine content will increase because the chlorine concentration increases as the seam depth increases. A plausible explanation is that the coal is in apparent equilibrium with the composition of the ground water associated with it, and the salinity of water (mainly due to alkali chlorides) increases with depth[4,5].

It is still not possible to give a clear account of the mode of combination of chlorine in coal for two main reasons. The first is the largely different characteristics of the coals examined, in fact, some authors have reported different chlorine compounds in different samples[6,7]. The second is the inability to achieve direct identification of these rare compounds in material as heterogeneous as coal. Therefore investigation of chlorine in coal has usually involved indirect methodologies, such as leaching or heating.

Early works, generally based on the study of the solubility of chlorine present in coal, followed by the characterization of the aqueous extracts obtained, suggested that chlorine is mostly present as alkali chlorides, mainly sodium chloride[8-10]. Nevertheless, the presence of halite or sylvite has not been revealed. In the most recent works, it has been proposed that chlorine

could be present as NaCl trapped in pores and fissures, or associated with the organic matter, either as chloride ions linked to coal by an ion exchange or covalently bonded to organic matter[7,11,12].

In spite of numerous published works, the mode of occurrence of chlorine in coals remains obscure. The aim of this paper is to reveal the presence of chlorine, its concentration and its chemical association in two high volatile bituminous coals from the Asturian basin.

## EXPERIMENTAL

The samples used were representative high volatile bituminous coals from the 'Mosquitera' and 'El Entrego' mines in the Asturian Central coalfield. They are raw coals with $\approx 50$ wt% ash yield (*Table 1*). For the densimetric separations, 1 kg of sample, ground to a particle size <5 mm, was used. The separation was carried out with four mixtures of xilol (commercial grade) and bromoform (Merck 98 % purity). Gas chromatography analysis revealed no chlorine was present in the liquids used. The specific gravities of mixtures were between 1.30 and 2.40 kg l$^{-1}$, and the ash yield in the separated coal fractions ranged from 3 to 90 wt % (*Table 1*). These fractions were then ground down to 0.212 mm.

The low temperature ash was obtained in a LTA-504 equipment for LFE Co. The sample (1 g) was oxidized using a radiofrequency power of 150 W and an oxygen flow of 15 ml min$^{-1}$ for four 6 h periods, with intermittent stirring. The proximate and ultimate analysis was carried out according to ISO standard methods.

For leaching, 5 g of sample, previous ground to <20 $\mu$m in a Retsch mill was used. Extractions were made by refluxing with 100 ml of boiling water for 48 h.