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A CALORIMETRIC STUDY OF THE IMMERSION
OF BITUMINOUS COAL IN LIQUIDS

by

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ABSTRACT

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Chemistry

The surface properties of coal greatly affect its use in industrial processes such as gasification, liquefaction and the use of coal slurries. In addition, such processes also involve reagent penetration into coal pores and the oxidative state of the coal surface. Reagent penetration into coal was examined by determining the heat and kinetics of immersion of Pocahontas No. 3 coal in water, methanol, a series of n-alkanes, and several cyclic and heterocyclic hydrocarbons. Results indicate that the heat of immersion is sensitive to the carbon chain length of the wetting liquid and its ability to hydrogen bond to coal. The time of immersion is insensitive to carbon chain length but is increased by the presence of nitrogen in a cyclic hydrocarbon.

The oxidation of both unextracted and extracted coal at 320°C was followed by immersional measurements in water.

The heat of immersion increased rapidly with oxidation time, leveling off after 3 hours of oxidation. Extraction with methanol or pyridine prior to oxidation and immersion lowered the time of immersion in water compared to the unextracted case. The oxidation of coal was also followed by x-ray photoelectron spectroscopy (XPS). The XPS oxygen/carbon ratios correlated linearly with the heats of immersion for the extracted, oxidized coals. Thus, XPS was shown to be a useful ancillary technique to heat of immersion for the study of coal surfaces.

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Chapter 1

INTRODUCTION

As the world's largest industrial nation, the United States consumes more energy per capita than any other nation. The majority of this energy demand is supplied by petroleum, a large portion of which is imported from abroad (1). Reliance upon foreign oil producers can be deleterious to the petroleum industry if the supply is suddenly stopped, as in the 1973 oil embargo by the oil-producers of the Middle East. One obvious way to negate this weakness is to turn to solid fuels, namely coal. The United States possesses 25-30 percent of the world's coal reserve, 70 percent of which still remains unmined (2). In 1985 alone, domestic mining operations produced approximately 864 million tons of coal and employed almost 150,000 people (3). Clearly, improved and increased use of coal will benefit not only the coal industry, but will also aid the United States in becoming independent of foreign energy sources.

The key to increasing the use of coal in industry today lies in streamlining coal utilization processes such as liquefaction, gasification and the use of coal slurries (4). The National Bureau of Standards recently surveyed (5) industrial, government and academic groups to determine key research needs for the coal industry. In general, the

survey noted a need for more data on the thermophysical properties of coal. Some specific recommendations of the N.B.S. included

1. developing reliable measurement techniques for heat capacity, thermal conductivity, and heat of wetting;
2. evaluating the effects of coal handling on the physical and chemical properties of coal; and,
3. developing theoretical models for both equilibrium and transport properties of coal with possible extension to structural properties such as porosity. Of particular interest to coal researchers is the interaction of coal with hydrocarbon liquids and with water.

In order to address the above recommendations, an understanding of the surface chemistry of coal is necessary. The objective of this study was to investigate the surface properties of unoxidized and oxidized coals via microcalorimetry and x-ray photoelectron spectroscopy (XPS). Specifically, the heats and times of immersion of Pocahontas No. 3 coal were determined in a homologous series of n-alkanes, in cyclic and heterocyclic hydrocarbon liquids, and in water. Furthermore, the effect of solvent extraction with methanol and pyridine was examined by measuring the heats of immersion in water as a function of oxidation time at 320°C for both extracted and unextracted coal. The XPS

O/C ratios of oxidized Pocahontas No. 3 were also determined. Information regarding the surface properties of extracted and unextracted coals prior to and following oxidation can be applied to the areas of coal flotation, liquefaction and gasification.

Chapter II

LITERATURE REVIEW

A. Coal Structure

1. Introduction

While coal is often termed a mineral resource, it is neither a crystalline solid nor an inorganic substance of definite composition (6). Coal is an organic rock formed from sedimentary plant remains which date from the Carboniferous period, 250 million years ago. In the ensuing millennia, the geological forces of heat and pressure as well as microbial action have transformed the carbonaceous sediment into a substance with a complex and varied structure (7). Microscopically coal consists primarily of macerals and subordinately of minerals. A maceral is any of several physically distinct portions of coal which were formed only from plant cells, cell walls and/or seeds. There are three main groupings of macerals, namely, vitrinite, liptinite, and inertinite. Macerals are chiefly classified according to reflectivity, density, and chemical reactivity. While the relative proportions of the different macerals vary from one coal to the next, the major maceral component in most coals is vitrinite. The mineral matter in coal is mainly due to the trapping of clays and other

impurities between macerals, although minerals may also be included within a maceral at some point in the coalification process (8).

Beyond the simple microscopic features of macerals and minerals, coal possesses several levels of structure. The primary structure of coal is its chemical composition, that is, the relative proportions of carbon, hydrogen, oxygen, and heteroatoms present in a given coal. The second level of coal structure is the macromolecular structure, the three-dimensional arrangement of coal moieties. Lastly, the third level of coal structure is the microporous fine structure of coals. It is this microporosity that leads to the molecular seive properties of coal and to large exothermic heats of wetting.

Coal is composed mainly of carbon, hydrogen and oxygen with small amounts of sulfur and nitrogen. The primary component of coal is carbon. The carbon content, among other properties, defines the rank of a coal. Low rank lignites, for example, contain 50-70 percent carbon and are relatively "young" coals. Sub-bituminous coals contain 70-75 percent carbon, whereas bituminous coals contain 75-95 percent carbon. Anthracites, the oldest coals, contain 95 percent carbon or greater. The chemical structure of the carbon in coals has been a subject of much controversy.

Chakrabartty and Berkowitz (9) suggested that coal was not aromatic, being composed of tricycloalkane and polyamantane systems. Their claim is based on the premise that hypochlorite oxidation of coal is restricted to sp^3 carbons. However, Van Krevelen (7) notes that both sp^3 and sp^2 carbons in the compound fluorescein are affected by hypochlorite oxidation. The question of aromaticity in coals is best solved by examining the hydrogen content of coal. As found by ^{13}C n.m.r., the hydrogen content of most coals, except anthracites, is 5-6 percent (10). Anthracites generally have a hydrogen content of 2 percent. Since the carbon content of coals increases with increasing rank and the hydrogen content remains essentially constant, one may only assume that aromaticity increases with increasing rank.

Coal also contains oxygen, sulfur and nitrogen. The oxygen in coal may exist in the form of water, inorganic minerals, or organic functional groups (11). In general, the amount of oxygen in a coal decreases with increasing rank. The major oxygen-containing functional group in coal is the ether group. Ether linkages are responsible for the initial stages of coal liquefaction (12).

The concentration of sulfur in coal is usually small, around 0.1-0.8 percent by weight. The presence of sulfur in coal is largely due to the inclusion of pyrite. Organic

sulfur is also present in the form of thiophenes (13). The nitrogen content of coal is 1-2 percent. Although little is known about the source of this nitrogen, it is thought to have originated in the plant tissues prior to coalification. It is generally held that the nitrogen in coal is incorporated into heterocyclic rings (11).

From a purely chemical point of view, coal seems to consist of clusters of aromatic and heteroaromatic rings, joined by aliphatic side chains and ether bridges (14). Whitehurst et al. (15) have proposed a representation of the functional groups in coal which is shown in Figure 1. The representation that they have developed shows the arrangement of the aromatic and aliphatic carbon clusters as well as the typical functional positions for oxygen, nitrogen and sulfur atoms. It should be noted that this representation is not meant to depict a true coal molecule. Rather, Figure 1 is a model which corresponds to experimentally observed results for bituminous coals in particular.

2. The Macromolecular Nature of Coal

Several different models for the macromolecular structure of coal have been developed. Most models were constructed to fit the results obtained by a certain

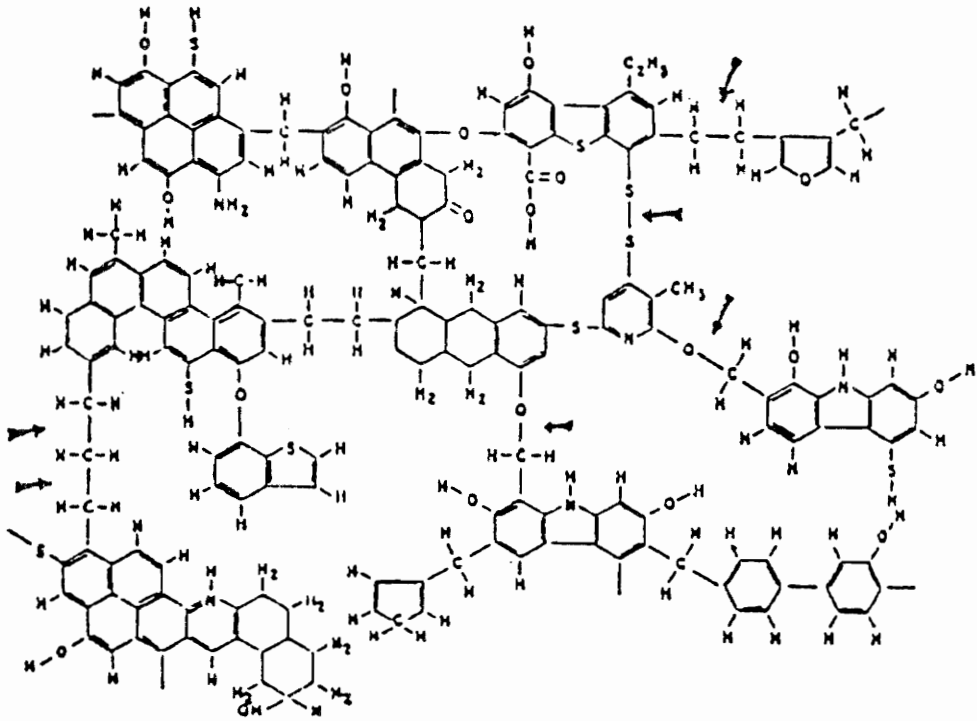


Figure 1. Representation of functional groups in coal (15).

experimental approach. One such model which is of historical importance is the micelle model. Evidence for a micellular model of coal structure evolved from extraction studies. Dryden (16) measured the intrinsic viscosity of ethylenediamine coal extracts. His results indicated spherical particles of colloidal dimensions, 20-70 nm in diameter. Furthermore, the chemical composition of the solubles and the parent coal were similar. This led Dryden to propose that coal possessed an insoluble matrix of strongly linked micelles closely associated with smaller, less strongly linked micelles.

Another model for the macromolecular structure of coal was developed by Vahrman (17). Although Vahrman's model also evolved from extraction studies on coal, the insoluble matrix was thought to consist of large, covalently bonded molecules. In addition to the insoluble matrix, Vahrman proposed a potentially soluble portion of smaller molecules, absorbed on the pore surfaces of coal. Evidence for such a model was derived from prolonged extraction studies of a bituminous coal using ethanol and benzene. Vahrman noted that the size of the extracted molecule did not govern the ease with which it was extracted. In fact, molecules of large critical dimensions emerged early. These molecules were thought to lie in pores of large diameter. Molecules

extracted with difficulty were thought to lie in narrow pores, into which solvent penetration was kinetically slow.

Two ideas which emerge from Vahrman's model were important in developing the present model of the macromolecular structure of coal. First, coal consists primarily of an insoluble matrix together with a substantial amount of smaller molecules. Second, the smaller molecules may lie within the macro-micro pore system of coal.

Most chemists now agree that coal is macromolecular in nature. Van Krevelen (7) stated a three part argument which provides evidence for the present macromolecular structure of coal. Firstly, coals are not soluble. Although some parts of coal will dissolve, as shown by Dryden (16) and Vahrman (17), the bulk of most coals is insoluble. This is consistent with a cross-linked macromolecular gel structure.

Secondly, coals behave as if they are large molecules being cleaved. This evidence is supplied by Van Krevelen (7) and is twofold. Hydrogenolysis of coal increased the amount of soluble material in coal, and this material is very similar to the material extracted from the unreacted coal. Similarly, mild oxidation of coal produced both aliphatic and aromatic carboxylic acids of low molecular weight.

Thirdly, coals swell. When contacted with a suitable

solvent, coals may increase their volume 80-100 percent (18). This observation has led to the application of polymer swelling theory. Flory (19) has related the swelling ratio of a polymer to the degree of polymer crosslinking and to the solubility parameter of the solvent. The fact that coals swell reveals the cross-linked, macromolecular nature of the insoluble coal matrix.

Sanada and Honda (20) have used Flory's approach to calculate the mean molecular weight per crosslinked unit of coal, M_c . Their results for M_c as a function of coal rank are shown in Figure 2. The value of M_c is nearly the same for lignites and sub-bituminous coals. For bituminous coals, however, the value of M_c is much higher and displays a maximum around 85 percent carbon. Sanada and Honda conclude then that bituminous coals have the most loosely cross-linked structure of all in the rank series.

Larsen et al. (21) have studied the swelling of a bituminous coal as a function of the solubility parameter of the solvent. Their results are shown in Figure 3. Of the non-polar solvents studied, those with a solubility parameter around $9.3 \text{ (cal/cm}^3)^{1/2}$ swelled the coal to the greatest extent. The coal exhibits even greater swelling in a polar solvent such as pyridine. Larsen et al. attribute the increased swelling in polar solvents to hydrogen

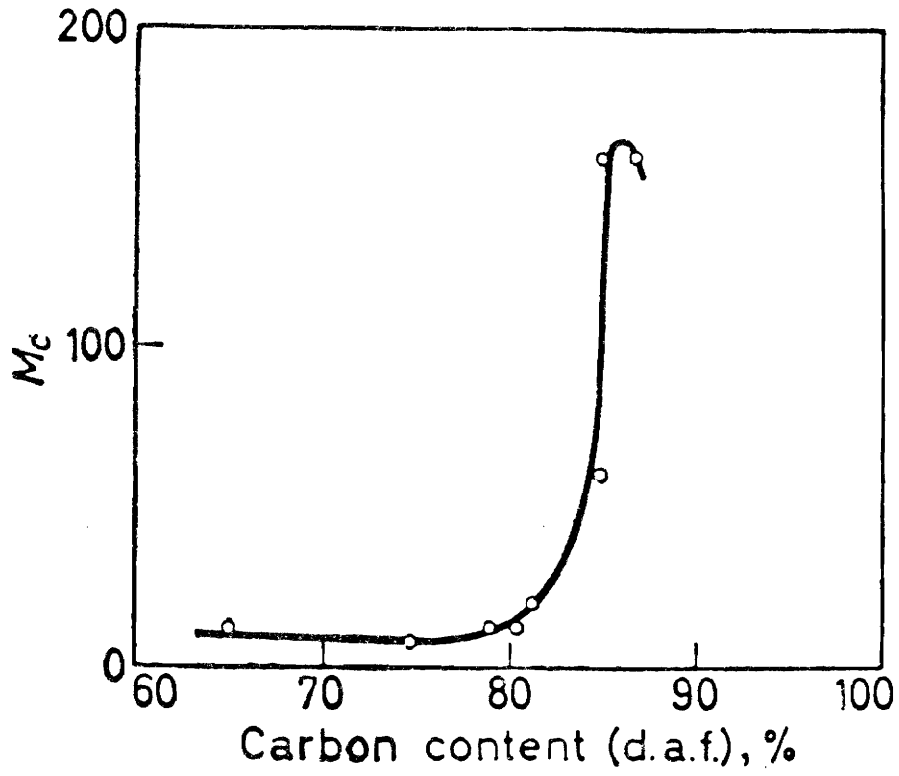


Figure 2. Mean molecular weight per crosslinked unit versus rank of coal (20).

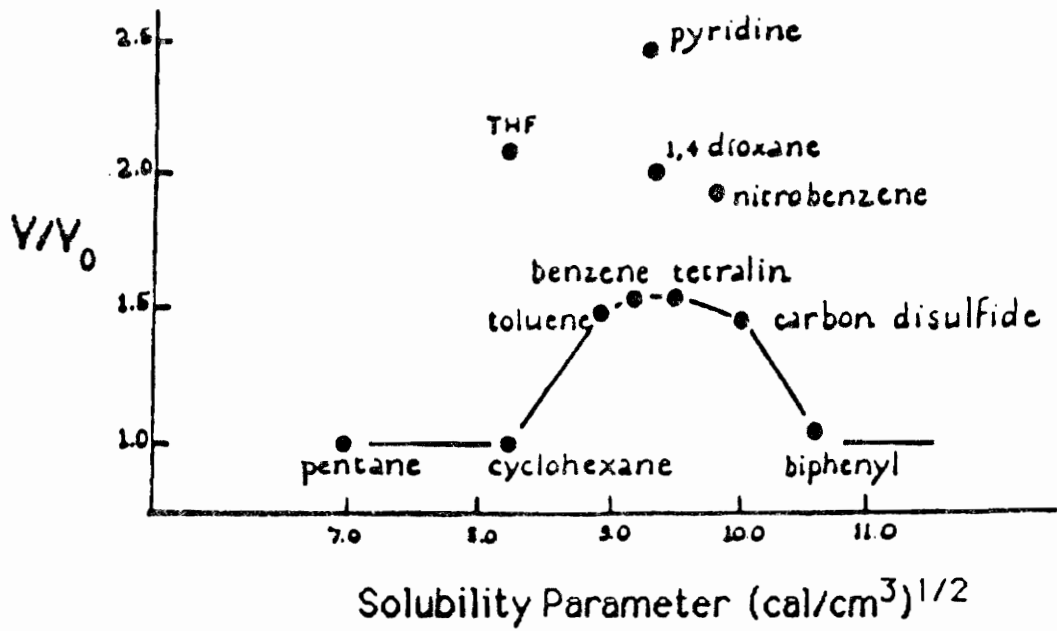


Figure 3. Swelling ratio of pyridine extracted Illinois No. 6 coal as a function of the non-polar solubility parameter of the swelling solvent (21).

bonding. A coal-coal hydrogen bond will be replaced by a coal-solvent hydrogen bond only if the coal-solvent hydrogen bond is stronger. Thus, the stronger the hydrogen bonds formed by a solvent, the more coal-coal hydrogen bonds it can replace. If the cross links in coal are hydrogen bonds, then the swelling ratio will be higher in a hydrogen bonding solvent.

Similarly, Marzec and Kisielow (22) have correlated extract yields with the electron-donor-acceptor (EDA) numbers of the extracting solvents. A solvent with a high electron-donor number gives a higher extract yield. The implications for coal structure is that the cross links between macromolecules are neither covalent nor dispersive, but specific polar interactions.

The present view of the macromolecular structure of coal can now be summarized. Coal consists of an insoluble, three-dimensional, cross linked matrix. Coal also possesses a substantial amount of smaller moleculars dispersed within the insoluble matrix of coal and adsorbed on the porous surfaces of coal. These smaller molecules are chemically similar to the macromolecules in the matrix. Although the swelling behavior of coal is consistent with a cross-linked polymer, coal is not a polymer in that there is no identical repeating unit. Rather, it is likely that there are a

variety of different subunits which constitute the insoluble coal matrix (23).

3. The Microporous Structure of Coal

Coal is a solid colloid possessing at any rank a certain porosity. It is to this porosity that coal owes the capacity to absorb gases and to develop exothermic heat of wetting (7). The porosity of coal governs its utilization in industrial processes such as gasification and liquefaction. Coal gasification involves reactions between gases and coal surfaces. Since most of the surface area of coal is located within the pores, reactions on the coal surface require the diffusion of reactant and product gases through the porous structures of coal (24). Similarly, coal liquefaction involves the imbibition of a hydrogen rich donor solvent into the coal structure. The presence of porosity greatly increases the rate of solvent uptake, thereby increasing the yield of liquefaction products (25).

A discussion of coal porosity carries with it other important parameters which must be examined. In order to characterize the porosity of a given coal, one needs to estimate the pore volume, surface area and pore size distribution.

The determination of pore volume requires the

measurement of both true and particle densities. The true density of coal is found by helium displacement. Helium, the smallest atom, is capable of filling all pores of diameter > 0.3 nm (7). The particle density of coal is the density of coal including cracks and pores. Particle densities are found by mercury displacement. The difference between mercury and helium densities is due to pore volume. For example, Zwietering and Van Krevelen (26) measured the pore volume of a bituminous coal using the above method. Their results indicate a pore volume of $0.134 \text{ cm}^3/\text{g}$.

Gan et al. (27) have studied the variation in helium density and pore volume with coal rank. Coals with 75-865 percent carbon show a minimum in helium density and a concomitant maximum in pore volume. Similarly, Toda (28) measured the densities of twelve Japanese coals. He reports a minimum in both helium and mercury densities for coals around 85 percent carbon.

The fact that coals possess porosity implies the presence of a large surface area. Unfortunately, there is no method for accurately determining the surface of area of coal (29). The surface area of a coal depends upon its rank and degree of porosity. Since surface areas are based on the adsorption of liquid or gaseous adsorbates, the temperature of adsorption and the physical nature of the

adsorbate also influence surface area values.

Gan et al. (27) determined the surface areas of American coals using nitrogen at 77 K and carbon dioxide at 298 K. Their results are shown in Figure 4. The surface areas calculated from nitrogen adsorption show a maximum around 75-85 percent carbon content. Conversely, the carbon dioxide surface areas display a minimum for coals of 75-85 percent carbon. Such behavior is due to the closure of smaller pores at the lower adsorption temperature (77K), resulting in smaller nitrogen surface areas (30).

Zwietering et al. (31) examined the surface areas of coal with respect to a change in pore volume. The pore volume of a British coal was artificially increased by heating the coal to 450°C under nitrogen gas. The surface area, calculated from nitrogen adsorption at 77 K, increased with an increase in pore volume.

The variation in surface area as a function of adsorption temperature was examined by Walker and Kini (32). They determined the carbon dioxide surface areas of six coals at 195 K and 298 K. In general, the surface area at 298 K was higher than at 195 K. The measurement of larger surface areas at higher temperatures supports the conclusion that adsorption is limited by pore closure at lower temperatures (30).

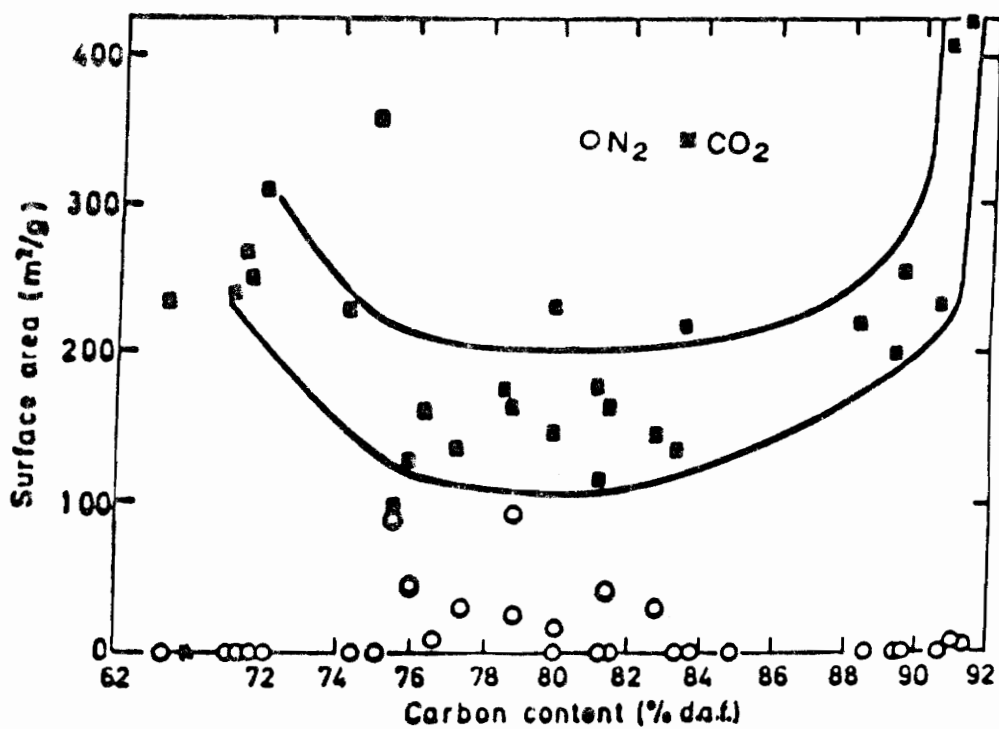


Figure 4. Variation of nitrogen and carbon dioxide surface areas of coals with carbon content (27).

The relationship between pore volume and surface area is not trivial. A large pore volume does not necessarily imply a large surface area (7). Pore surface areas are related to pore size; total surface areas are related to the pore size distribution of the coal. Pore size distributions are generally determined by following mercury penetration into coal as a function of applied pressure. The maximum pressure, P , required to force mercury into a pore of radius, r , is given by the relation

$$P = -2\gamma\cos\theta/r \quad [2-1]$$

where γ is the surface tension of mercury and θ is the contact angle between mercury and the pore wall.

Zwietering and Van Krevelen (26) determined the pore size distribution of a bituminous coal using equation 2-1. They determined that a maximum existed in the number of pores of radius 30-40 nm. Similarly, Gan et al. (27) determined the pore size distribution of American coals. They classified the porosity of coal into three groups:

1. pores with diameter > 30 nm, macropores;
2. pores with diameters of 30-1.2 nm, mesopores;
and,
3. pores with diameters < 1.2 nm, micropores.

Moreover, they attribute the porosity of lower rank coals primarily to macropores. Coals in the range of 70-84 percent

carbon owe their porosity mainly to meso- and micropores, while in the higher rank coals, microporosity predominates. In bituminous and anthracite coals, then, the majority of the surface area is due to the presence of micropores.

B. Coal Oxidation

The oxidation of coal is known to have a marked effect on various utilization processes including flotation, liquefaction, pyrolysis, and gasification. In addition, self-heating of coal during storage is attributed to the oxidized state of the coal surface.

Bouwman and Freriks have examined the effect of low temperature oxidation on coal stored in above ground piles (33). After examining the oxidized coals using infrared spectroscopy, they postulated a mechanism for coal oxidation which is illustrated in Figure 5. One aspect of this mechanism is that as one product molecule leaves the surface, one or more reactive sites are uncovered. Furthermore, this mechanism occurred at a faster rate for coals buried more deeply in the pile. Thus coal deep within the pile is more susceptible to self-heating and is at a higher effective temperature.

One physical method for determining the degree of oxidation of a coal is flotation. Coals are generally

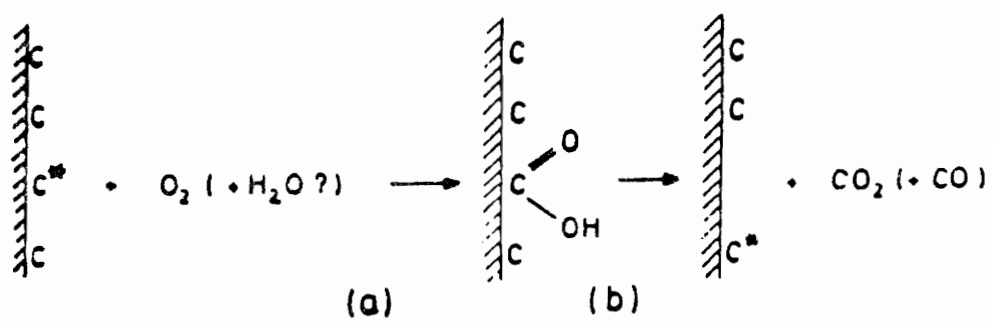


Figure 5. A proposed mechanism of coal oxidation (33).

hydrophobic. Higher rank coals in particular will float on water. Iskra and Laskowski (34) measured the flotation of coal in 0.5 N potassium chloride solutions as a function of oxidation time and the pH of the solution. They found that flotation yields decreased with oxidation time at various temperatures. Flotation yields also decreased with a decrease in the pH of the salt solution. Their results show the sensitivity of a simple physical test such as salt flotation to the oxidative state of the coal surface.

Changes in the sorption properties of coal were examined by Youssef and El-Wakil (35) as a function of storage in air. The sorption of water vapor on coal was increased as a result of aging in air, while the sorption of nitrogen gas decreased. Their conclusion is that the increase in water sorption is due to changes in the surface polarity. Moreover, nitrogen sorption is inhibited by surface bound oxygen.

Recently, Phillips et al. (36) monitored the oxidation of a Virginia coal as a function of oxidation temperature using microcalorimetry and x-ray photoelectron spectroscopy (XPS). The heat of immersion of coal in water was found to increase with increasing oxidation temperature. The surface oxygen to carbon ratios, as determined by XPS, showed a similar trend. The carbon-oxygen species detected on the

surface were C-O, C=O and O-C=O. Substantial amounts of heat were released upon wetting the oxidized coal, up to 100J/g of coal. This result accentuates the role of oxidation in the self-heating and self-ignition of coal.

Clark and Wilson have evaluated the applicability of x-ray photoelectron spectroscopy (XPS) to the study of coal surfaces (37). A part of this evaluation was to monitor the effect of ultraviolet radiation on the oxidation of coal. The XPS results show a dramatic increase in the oxygen 1s signal with increased exposure to ultraviolet light in air. Oxidation of carbon, as shown by the carbon 1s peak, was apparent after only 30 min of irradiation.

Smyrl and Fuller (38) have investigated the oxidation of a sub-bituminous coal using diffuse reflectance infrared Fourier - transform spectroscopy (DRIFT). Their results show an increase in oxygen containing functional groups for the oxidized coal over the unoxidized coal. Moreover, the utility of DRIFT over KBr pellets is emphasized. DRIFT requires no sample preparation and allows the in situ monitoring of coal oxidation.

Coal pyrolysis, a method of depolymerizing coal into gases and hydrocarbon liquids, is another process affected by coal oxidation. It has been shown (39) that mild oxidation of coal results in a decrease in liquid

hydrocarbon yields. This behavior is probably due to the formation of ether linkages within the coal, which produces a three-dimensional aggregate that resists swelling. The inability to swell is also known to effect coking properties and liquefaction yields (25).

Coal gasification, on the other hand, makes use of oxidatively induced crosslinks. Gouker and Liotta (40) have investigated the use of both air and chemical oxidation to eliminate the plastic properties of coal, thereby making it suitable for high pressure gasification. Their results indicate that only caustic oxidation (KOH) is severe enough to convert a thermoplastic coal to a thermosetting coal. Analysis using ^{13}C n.m.r. showed a substantial increase in the number of carboxyl and ether groups on the coal surface. The carboxyl groups serve as precursors for crosslinks between coal macromolecules.

C. Heats of Immersion

Most interactions between a solid surface and a liquid involve the production or consumption of heat. If a bare solid is immersed in a pure liquid then the heat produced is termed the heat of immersion. Heats of immersion are sensitive to the nature of the solid-liquid interaction. For example, the physical adsorption of a non-polar liquid

on a non-polar surface will yield a much different heat than the physical adsorption of a polar liquid on a polar surface. Both of these phenomena are distinguishable from the chemisorption of a liquid on a solid surface, since chemisorption involves bond formation between adsorbate and adsorbent. For porous solids, other factors besides surface polarity or reactivity may be important. Specifically, pore dimensions and the size of the wetting molecule may influence not only the amount of heat evolved but also the time required for total heat evolution. The time required for total heat evolution is termed the time of immersion.

Microcalorimetry is a thermodynamic technique which can measure both heats and times of immersion. Microcalorimetry, so named because of the small amounts of heat detectable, was first developed by Tian in 1939. In 1948, Calvet modified Tian's approach by implementing the twin or differential mode of operation (41). Since then microcalorimetry has been used to study many solid surfaces including clays, carbon blacks, and coals.

Chessick and Zettlemyer (42) have measured the heats of immersion of attapulgite clay in butylamine. By immersing both bare clay samples and clay samples partially precovered with butylamine vapor, the site energy distribution of acid exchange sites was developed.

Wade and Hackerman (43) measured the heats of immersion of kaolinite and calcite in water as a function of outgassing temperature. They discovered a discontinuity in the heat of immersion of kaolinite when outgassed at 360°C. This temperature corresponds to the dehydration of surface hydroxyl groups on kaolinite. The heat of immersion of calcite was independent of outgassing temperature up to 300°C at which point the calcite was converted to calcium oxide, CaO.

Immersional measurements on clays generally represent the study of specific interactions between polar surfaces and polar adsorbates. Non-polar surfaces such as carbon blacks and graphite, however, present quite a different system. Two approaches are taken to the study of carbon products: measure the heat of immersion as a function of some property of the wetting liquid (length, bulk) or measure the heat of immersion of a modified surface (oxidation, precoverage).

Robert and Brusset (44) examined three commercial carbon blacks using a Calvet microcalorimeter. The carbon blacks were immersed in a homologous series of n-alkanes. Graphon, a graphitized carbon black, exhibited a large increase in the heat of immersion with an increase in alkane chain length. Everett and Findenegg (45) as well as Clint

et al. (46) observed a similar phenomenon. The rationale for such behavior is as follows: at a given experimental temperature, the larger alkanes are closer to their melting (fusion) points. The proximity of a solid surface causes the larger alkanes to exhibit solid-like properties, i.e., ordering. This effect leads to a greater energy loss upon immersion compared with simple non-specific adsorption. The heat of wetting of alkanes on ungraphitized carbon blacks displays no such trend, presumably due to the lack of a homogeneous graphitized surface.

Barton et al. (47) evaluated the effect of n-alkanol and n-alkane chain length on the heat of immersion of a porous carbon formed from polyvinylidene chloride. As a result of the porous nature of this adsorbent, the heat of immersion decreased with an increase in carbon chain length. This behavior is opposite that observed by Clint et al. (46). Barton concludes that for a porous adsorbent, partial solidification of the adsorbate by lateral interactions does not occur. Barton also examined the heat of immersion of this carbon in branched chain alkanes. The results indicate a decrease in the heat of immersion with increased branching. Here, the porous nature of the carbon is selectively excluding larger molecules from accessing part of the surface.

The heats of immersion of carbon blacks are dependent upon surface homogeneity and porosity as well as the nature of the wetting liquid. This behavior offers good opportunity for comparison with the immersional behavior of coals, which are porous and heterogeneous.

Glanville and Wightman (48) have examined the immersional behavior of Pocahontas No. 3 coal, a bituminous coal, in methanol-water mixtures and a variety of other liquids. The heat of immersion was found to increase non-linearly with an increase in the methanol composition of the wetting solution. Figure 6 shows the rectilinear relationship of heat of immersion and the surface tension of the wetting solution. As the surface tension of the wetting solution increases, the heat of immersion of coal decreases.

In addition the heats and times of immersion of Pocahontas No. 3 coal were determined in various liquids. These results are shown in Table 1. The heat of immersion in methanol and n-butanol are similar, but methanol was able to release the heat in 30 minutes. Nine hours were required for total heat release to occur in n-butanol. This result indicates the role of liquid bulkiness or cross-sectional area in the wetting of porous solids. It is also interesting to note that tetralin gave a heat of immersion almost four times as great as that of decalin. Furthermore,

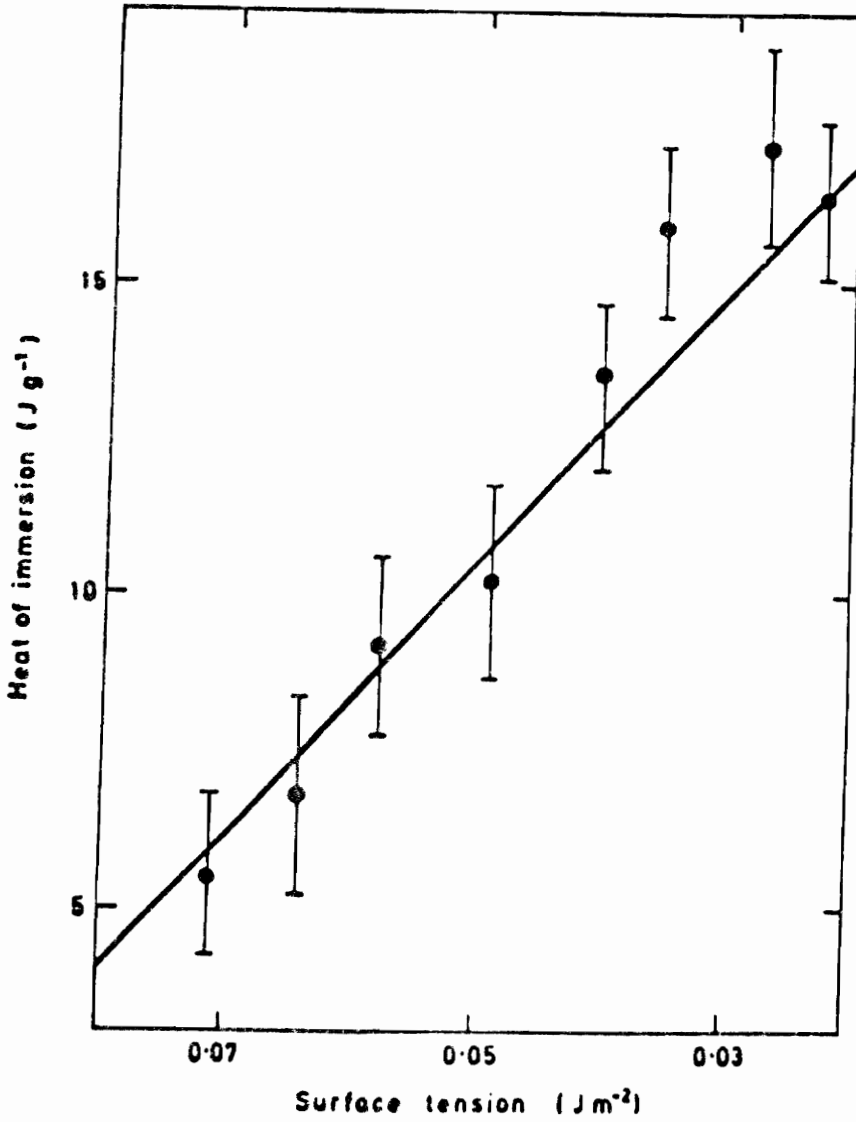


Figure 6. Heats of immersion of Pocahontas No. 3 coal dust in methanol / water mixtures as a function of surface tension (48).

TABLE 1

HEATS OF IMMERSION OF POCAHONTAS NO. 3 COAL DUST IN
VARIOUS LIQUIDS AND THEIR APPROXIMATE RELEASE TIMES (48)

Liquid	Heat of Immersion <u>(J g⁻¹)</u>	Approximate time to reach <u>equilibrium (h)</u>
Methanol	16.2	0.4
Ethanol	15	4
Straight-chain Propanol	14	7
Straight-chain Butanol	15	9
Methylene Chloride	21	2
Pyridine	15	2
Tetrahydrofuran	11	1.5
Tetralin	7.6	0.6
Water	5.4	0.8
Ethylene Glycol	5.0	3
Decalin	2.1	2.5
Hexane	3.7	2.7

the heat was evolved almost four times as fast. This explains why tetralin is considered a better solvent for coal liquefaction than decalin, even though decalin should be a richer source of hydrogen.

Larsen and Kuemmerle (49), upon studying the immersion of Bruceton coal in several liquids, have discovered an unusual temperature dependence for the heat of immersion in tetralin. The heats of immersion in tetralin below 32°C are exothermic. However, above 32°C the heats of immersion become endothermic. Larsen concludes that at higher temperatures adsorbate binding is entropy controlled. Since tetralin loses degrees of freedom upon adsorbing to the surface, the structure of coal must be disrupted to account for the entropy change.

The effect of rank, particle size and mineral matter content on the heat of immersion in water has been investigated by Fuller (50). Lower rank coals gave higher heats of immersion in water due to their more loosely bound structure and higher heteroatom content. The amount of heat evolved was greater for small size particles of any rank. Furthermore, the rate of heat release decreases with a decrease in particle size. The heat of immersion in water was greater for mineral rich samples than for mineral deficient ones, due to the greater polarity of the minerals.

Widyani and Wightman (51) have examined the heats and times of immersion of Pocahontas No. 3 coal in a series of n-alkanols. Contrary to the results of Clint et al. (46) the heat of immersion decreased non-linearly with an increase in n-alkanol chain length. This result indicates the progressive exclusion of adsorbate molecules from the pores of coal as the adsorbate molecules become longer. The effect of chain length on the time of immersion was to produce a maximum in specific immersion time for n-butanol. This result is shown in Figure 7. Methanol penetrates the pores of coal easily, therefore the kinetics of immersion are fast. Butanol does not penetrate as easily as methanol and the kinetics of immersion are slow. Dodecanol does not penetrate the porous structure of coal and therefore the kinetics of immersion are fast, but the overall heat of immersion is low.

A similar trend was found by Glanville et al. (52) for sub-bituminous and bituminous coals. Of the four coals studied, all four show a maximum in the time of immersion for n-butanol. Moreover, this study incorporates the effect of molecular bulk on the heat and time of immersion. Table II shows the heats and times of immersion of a Wyodak coal (sub-bituminous) in butanol isomers. The bulkiest molecule,

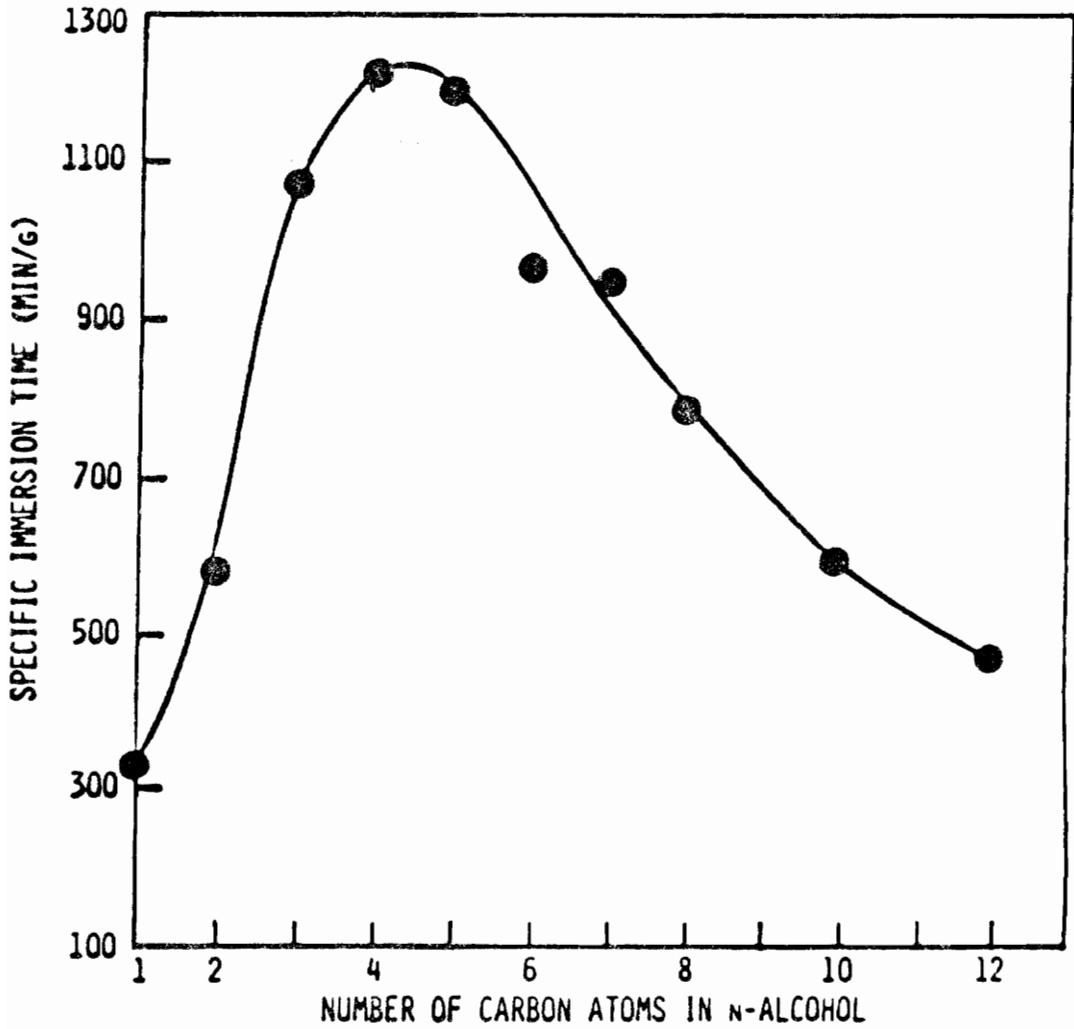


Figure 7. Kinetics of immersion of Pocahontas No. 3 coal in n-alcohols (51).

TABLE II

HEATS OF IMMERSION AND TIMES TO REACH THERMAL EQUILIBRIUM
FOR WYODAK NO. 1 COAL IN BUTANOL ISOMERS (52)

<u>Isomer</u>	Heat of Immersion <u>(J/g⁻¹)</u>	Approximate time to reach <u>equilibrium (h)</u>
n-Butanol	91	9
sec-Butanol	41	5
t-Butanol	15	2

tert-butanol, exhibits the shortest immersion time and therefore the lowest heat of immersion.

Nordon and Bainbridge (53) have evaluated the effect of moisture content on the heat of immersion of an Australian coal in water. The results indicate a decrease in the heat of immersion with increased water content of the coal. This supports the practical observation that a normal moist coal (65 percent relative humidity) will not undergo significant self-heating.

Phillips et al. (36) have measured the heat of immersion of Virginia-C coal in water as a function of oxidation temperature. For coals heated at various temperatures for 24 hours, the heats of immersion in water were the same up to 150°C. Coals heated above this temperature display a dramatic increase in the heat of immersion. There is a fifty-fold increase in the heat of immersion of the coal heated to 320°C over the unheated coal.

D. X-ray Photoelectron Spectroscopy

While x-ray photoelectron spectroscopy (XPS) is a well known surface sensitive technique, its potential application to coal science has not been realized.

Typically, XPS has been used to determine carbon,

nitrogen, and sulfur in coal (54). Good correlation between XPS results and ultimate chemical analyses have been found for these elements. Perhaps the most promising use of XPS is for oxygen determination in coal. Oxygen in coal is generally determined by difference, a method subject to cumulative errors. Clark and Wilson (37) have found XPS oxygen values to be higher than bulk elemental analyses, probably owing to the presence of more oxygen on the surface relative to the bulk.

Perhaps more useful than percent elemental composition data is the information XPS can yield with regard to the bonding environment of the analyte specie. As mentioned above, Phillips et al. (36) have used XPS results to complement thermodynamic results in the study of oxidized coals. Curve-fitting, a computer operation which separates composite XPS spectra into individual peaks, has allowed the determination of the carbon-oxygen species present under the carbon 1s photopeak. For the carbon 1s photopeak of an oxidized coal, Phillips et al. identified C-O, C=O and O-C=O groups on the coal surface. Such information supports the conclusion of Bouwman and Freriks (33) that coal oxidation proceeds via the carboxyl functionality.

Chapter III

EXPERIMENTAL

A. Materials and Reagents

1. Coal

The coal for this study was obtained from the Pocahontas #3 seam in McDowell County, WV. The coal was previously crushed and screened to -325 mesh U.S. (< 44 μm particle size). The proximate and ultimate analyses of this coal are given in Table III. The coal was stored under air in a tightly closed glass container.

2. Liquids

The n-alkanes octane through nonadecane as well as 1-methylnaphthalene, 1,2,3,4-tetrahydroquinoline, quinoline, tetralin, and pyridine were all obtained from the Aldrich Chemical Company. The liquids were of reagent grade and were used without further purification. Deionized water was prepared in the laboratory by passing tap water through commercially available deionization columns. The water was stored in a plastic carboy until needed.

TABLE III

PROXIMATE AND ULTIMATE ANALYSES OF POCAHONTAS NO. 3 COAL

Proximate Analysis (wt%, as-received-basis)

moisture	1.04
ash	5.0
volatile matter	17.0
fixed carbon	77.0

Ultimate analysis (wt%, as-received-basis)

carbon	84.75
hydrogen	4.6
nitrogen	0.97
chlorine	0.08
sulfur	0.61
ash	5.0
moisture	1.04
oxygen (by difference)	2.95

B. Procedures

1. Soxhlet Extraction

In order to determine the effect of solvent extraction on the heat of immersion and oxidation of coal, Soxhlet extraction was employed using methanol and pyridine. The procedure followed was identical for both solvents. Approximately 5 g. of coal was placed in a paper extraction thimble and situated in the Soxhlet apparatus. 200 ml. of the solvent (methanol or pyridine) were placed in a round bottom flask and attached to the Soxhlet extractor fitted with a reflux condenser. The solvent was refluxed for 24 hours. After refluxing, the coal was removed from the extractor and allowed to air dry for 24 hours. This was followed by vacuum drying at 10^{-4} - 10^{-5} torr for 24 hours. The methanol used in the extraction was nearly colorless after 24 hours of refluxing while the pyridine was opaque.

2. Coal Oxidation

Three types of coal were oxidized for analysis:

- (1) Raw or parent coal as taken from the laboratory container;
- (2) Methanol extracted and dried coal; and,
- (3) Pyridine extracted and dried coal.

For the oxidation study, then 0.5 g. samples of each of the

coals were weighed into 100ml pyrex beakers. The beakers were tapped lightly on the benchtop to distribute the powder evenly. The beakers were placed in a force-air oven at 320°C. The samples were removed at various times from 10 minutes up to 20 hours. It should be noted that all three types of coal were not oxidized at the same time, and therefore the times at which samples were removed differed. However, the procedure was otherwise identical for all three cases.

C. Heat and Time of Immersion Determinations

1. Calvet Microcalorimeter

The heats and times of immersion of Pocahontas #3 coal powder in a series of n-alkanes (C8-C19), in methanol, and in cyclic and heterocyclic hydrocarbons (tetralin, 1-methylnaphthlene, pyridine, quinoline, 1,2,3,4-tetrahydroquinoline) as well as the heats and times of immersion of the oxidized coal powders in water were made with a Calvet MS-70 microcalorimeter operated at 36.5°C.

A schematic presentation of the Calvet MS-70 is shown in Figure 8. The calorimeter has four cells connected electrically into two pairs. Each cell is surrounded in radial fashion by an array of thermocouples. The electrical connection between a pair of cells is such that should a

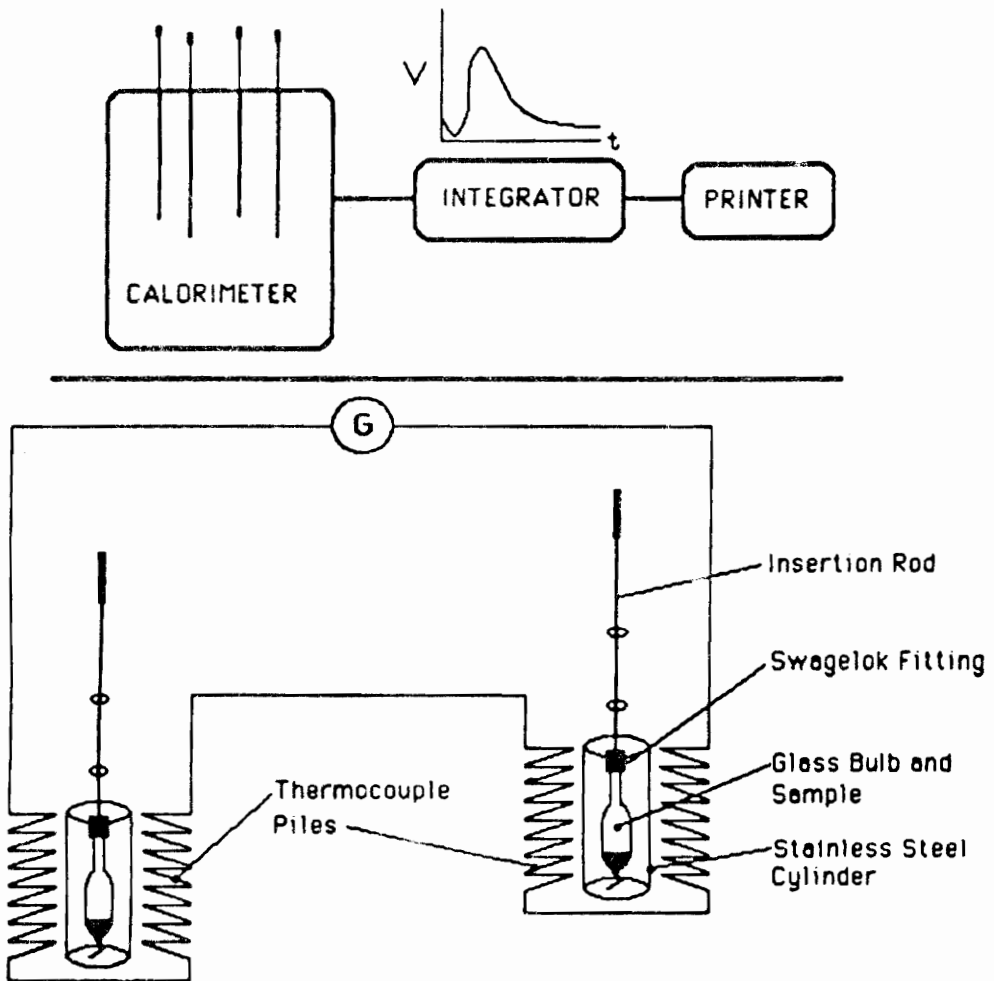


Figure 8. Schematic diagram of the Calvet MS-70 microcalorimeter and sample cells.

change in temperature occur within the calorimeter, the voltage produced by one cell is nulled by the voltage produced by the other cell of the pair. When only one cell of a pair is heated or cooled, an electrical imbalance is created which causes a current to flow. The voltage and direction of current flow reflect the magnitude and type of thermal effect which created it. The result is that for any given heat of immersion determination, one cell is a thermal reference while the other is the site of heat change. The voltage produced by the paired cells is amplified and integrated over time to yield an arbitrary quantity proportional to the amount of heat released (or consumed) by a cell. The integrated area is displayed sequentially by a printer attached to the integrator.

Since the calorimeter output is an arbitrary quantity, it must be calibrated with a known heat source. This is accomplished by passing a known current (I) through a precision resistance (R) for a given period of time (t). The resulting heat is divided by the quantity indicated by the printer (number of counts, C) to give a corresponding cell sensitivity (S). The following equation was used to calculate the cell sensitivities for this study:

$$S = I^2Rt/C \text{ (Joules/count)} \quad [3.1]$$

The sensitivity values determined for the four cells are

given in Table IV.

The Calvet microcalorimeter is a very sensitive instrument capable of detecting quantities of heat on the order of microjoule. However, in order to achieve a practical precision of 5 to 10 percent, it is desirable to measure thermal effects which produce a total of at least 0.01 Joules.

2. Immersional measurements

To measure the heat of immersion of coal in a given liquid, quadruplicate samples were prepared by weighing the coal into small pyrex bulbs (ca. 3.5 X 0.75 cm) with breakable tips. 50 mg samples were used for immersion in the hydrocarbons. Due to the long immersion times required, 25 mg samples of the oxidized coals were prepared for immersion in water. The bulbs were attached to a vacuum line and evacuated at 10^{-4} torr for 2 hours. After sealing the glass bulbs under vacuum, they were attached to the calorimeter insertion rods with modified Swagelok fittings. A stainless steel cylinder containing 5 ml of the wetting liquid was placed around each sample bulb forming a sealed unit at the bottom of each insertion rod. The entire assembly was wiped with acetone to remove foreign debris and placed in the microcalorimeter overnight to achieve thermal

TABLE IV

CELL SENSITIVITIES FOR THE CALVET MS-70 MICROCALORIMETER

<u>Cell</u>	<u>Sensitivity (Joules/count)</u>
1	$2.066 \times 10^{-3} \pm 0.006 \times 10^{-3}$
2	$2.125 \times 10^{-3} \pm 0.010 \times 10^{-3}$
3	$2.082 \times 10^{-3} \pm 0.006 \times 10^{-3}$
4	$2.154 \times 10^{-3} \pm 0.012 \times 10^{-3}$

equilibrium.

The following day, the integrator was reset and the signal from the calorimeter was integrated before breaking a sample bulb. If after 15 minutes the printer indicated no heat evolution, the calorimeter was assumed to be at steady state and the first sample was then broken by pressing the plunger at the end of the insertion rod. The electrical signal produced by the heat change in the calorimeter was monitored until the printout had repeated the same number six times, i.e., steady state was re-attained. This condition is known as baseline and occurs when $< 400 \mu\text{J}$ of heat are liberated over a 10 minute period. The time elapsed from breaking the sample to attaining baseline is termed the time of immersion. The specific time of immersion is simply the time of immersion taken on a per gram of solid basis. After breaking the first sample and achieving baseline, the second sample was immersed and so on. Though the Calvet microcalorimeter is generally very stable, problems in re-attaining steady state (i.e. baseline drift) are minimized by restricting the time of immersion to less than 3 hours by varying experimental parameters.

To complete a heat of immersion determination, it is necessary to immerse a set of four empty bulbs in each liquid to determine the heat of empty bulb breaking in each

cell. If the heat of empty bulb breaking was exothermic, it was subtracted from the heat of immersion of the sample. If the heat of empty bulb breaking was endothermic, it was added to the heat of immersion of the sample. The heat of immersion (ΔH_{imm}) of a sample in a given cell was determined by the relation

$$\Delta H_{imm} = (C_s \pm C_b) S_c / W \quad [3.2]$$

where C_s is the number of sample counts, C_b is the number of empty bulb counts, S_c is the sensitivity of the cell in Joules/count, and W is the weight of the coal in grams.

D. X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy, or XPS, is a surface sensitive technique which typically analyzes the top 5 nm of a solid surface. XPS involves measuring the kinetic energy of electrons ejected by x-ray bombardment. A schematic diagram of the XPS spectrometer is shown in Figure 9. The kinetic energy (K.E.) of an electron is related to the binding energy (B.E.) of the electron and to the x-ray energy which ejected it by the equation

$$h\nu = B.E. + K.E. + \phi \quad [3.3]$$

where $h\nu$ is the x-ray energy and ϕ is an instrumental correction which includes sample charging. Since the binding energy of an electron is unique for a given element

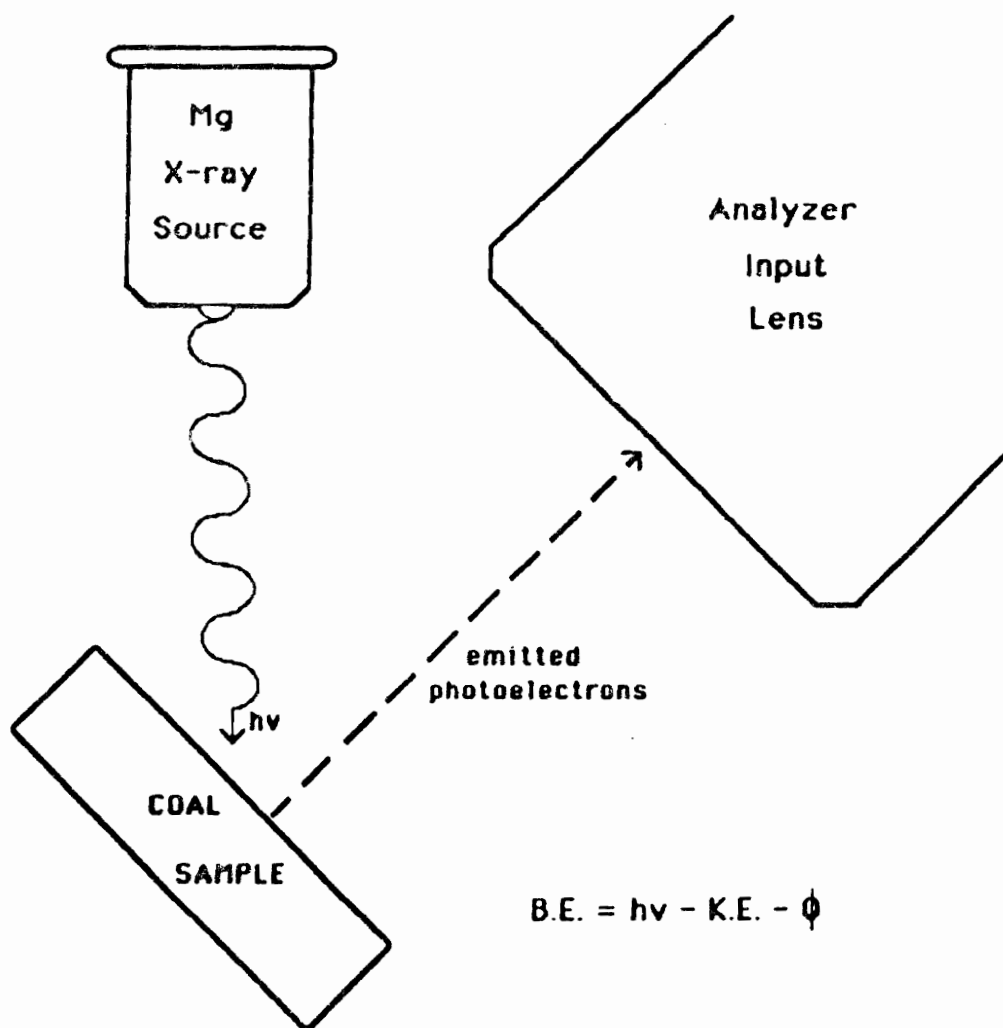


Figure 9. Schematic diagram of XPS analyzer.

in a given environment, one can identify the atomic species present in a solid surface.

A Perkin-Elmer PHI 5300 spectrometer was used in the XPS studies. This spectrometer has a Mg achromatic x-ray source operated at 14 kV. The system pressure was approximately 10^{-8} torr. The coal powder was mounted on double stick tape attached to a stainless steel sample holder. Spectra were obtained for the carbon 1s and oxygen 1s regions for all oxidized coals and also for the unoxidized coal. From these spectra, O/C ratios were calculated and related to oxidation time at 320°C. Spectra were also obtained for the nitrogen 1s region of the pyridine extracted coal.

Using a Perkin-Elmer Model 0.8 software package, the carbon 1s spectra of all the coal samples were curve fitted to determine the percent contribution of the C-C, C-O, C=O, and O=C-O subpeaks to the total carbon photopeak.

Chapter IV

RESULTS AND DISCUSSION

A. Immersion of Pocahontas No. 3 Coal in n-Alkanes

1. Heat of Immersion

Figure 10 illustrates the effect of n-alkane chain length on the heat of immersion of Pocahontas No. 3 coal. The heat of immersion shows an initial decrease with increasing carbon chain length, which then levels off after n-tridecane. This decrease is the opposite of the result obtained for the immersion of non-porous Graphon (44,46) in n-alkanes which displays an increasing heat of immersion at 25°C as chain length increases. This latter result is presumably due to structural changes in the liquid phase near the energetically homogeneous surface of Graphon (45). The lack of a homogeneous coal surface appears to prevent significant ordering of adsorbate molecules upon immersion. This explains why the heats of immersion of coal do not increase with an increase in n-alkane carbon chain length.

However, besides being heterogeneous, coal is also porous. Since a large portion of the surface area of a coal is internal, pore size may prohibit certain adsorbate molecules from accessing the internal surface of coal. Gan et al. (27) note that in bituminous coals, both meso- and

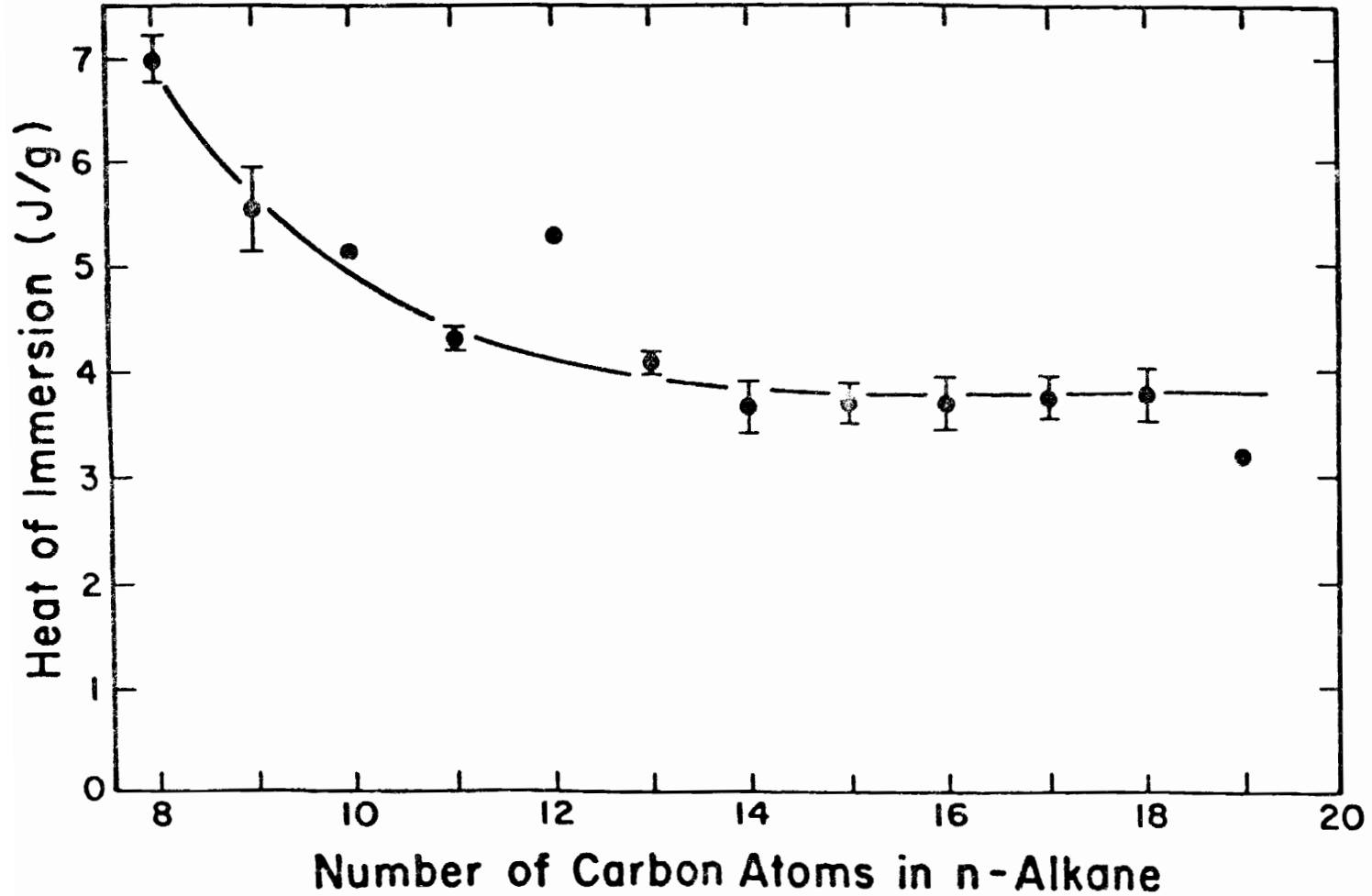


Figure 10. Heat of immersion of Pocahontas No. 3 coal in n-alkanes versus carbon number of the n-alkane.

microporosity predominate. Most of the pores in Pocahontas No. 3 then are < 1.5 nm in diameter. Thus, as the n-alkane becomes longer it is progressively excluded from more and more internal surface area. The result is a decrease in the heat of immersion. The fact that the heat of immersion levels off after n-tridecane indicates that the porous network of Pocahontas No. 3 excludes all n-alkanes longer than n-tridecane from the same amount of the internal surface.

Similarly, the heat of immersion of Pocahontas No. 3 in n-alkanols decreased non-linearly with increasing n-alkanol chain length (51). While the n-alkanol study was done with C1 through C12 alcohols, this study was done with C8 through C19 alkanes. In the range of similar chain length (C8 through C12) the heats of immersion are comparable for both n-alkanols (6-8 J/g) and n-alkanes (5-7 J/g). This suggests that the heat of immersion is governed principally by the length of the adsorbate molecule and that the hydroxyl functionality plays little or no role in determining the heat of immersion in longer alkanols. This result is consistent with the low oxygen (polar) content of the bituminous coal.

The number of carbon atoms in an n-alkane is roughly a measure of molecular length and as such is a one-

dimensional property of the molecule. However, if pore size governs the penetration of adsorbate molecules into coal, then the heat of immersion should be more closely related to molecular bulk rather than length. One measure of the molecular bulk on an n-alkane is the molarity of the liquid. Figure 11 illustrates the relationship between the heat of immersion and the molarity of the n-alkane. The heat of immersion increases as the molarity of the liquid increases. The relationship of heat of immersion to molarity appears more linear than the relationship of heat of immersion to chain length. The molecular volume of a liquid is inversely related to its molarity. A high molarity indicates a large number of moles (molecules) per unit volume of liquid and thus a small molecular volume. The results in Figure 11 support the conclusion that the pores of coal exclude adsorbate molecules on the basis of size and thereby limit the heat of immersion by limiting the surface area available to the wetting n-alkane.

2. Time of Immersion

Figure 12 shows the effect of n-alkane chain length on the specific time of immersion of Pocahontas No. 3 coal. With the exception of octane, the specific immersion time is roughly the same for all the n-alkanes. This is a

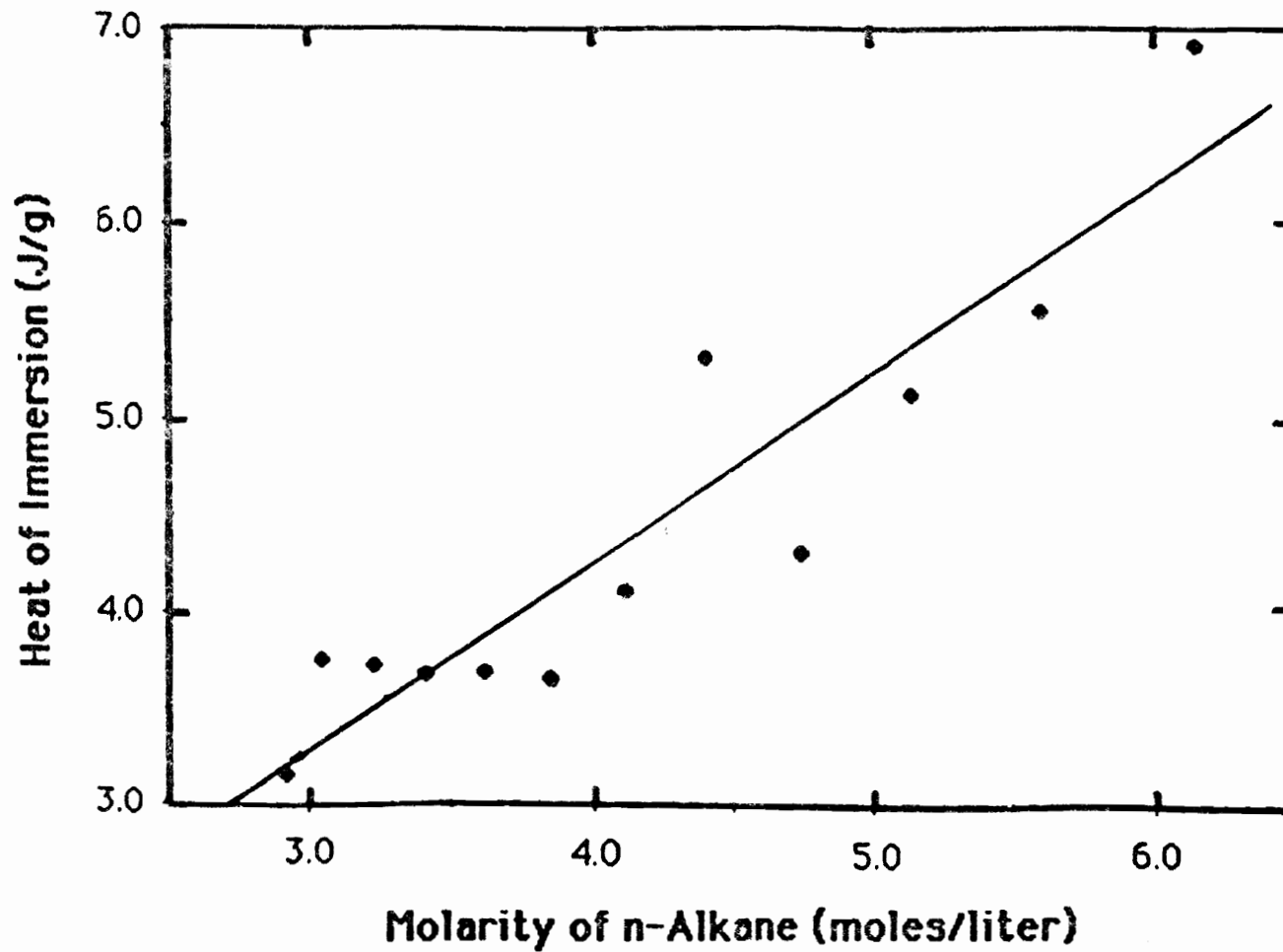


Figure 11. Heat of immersion of Pocahontas No. 3 coal in n-alkanes versus the molarity of the n-alkane.

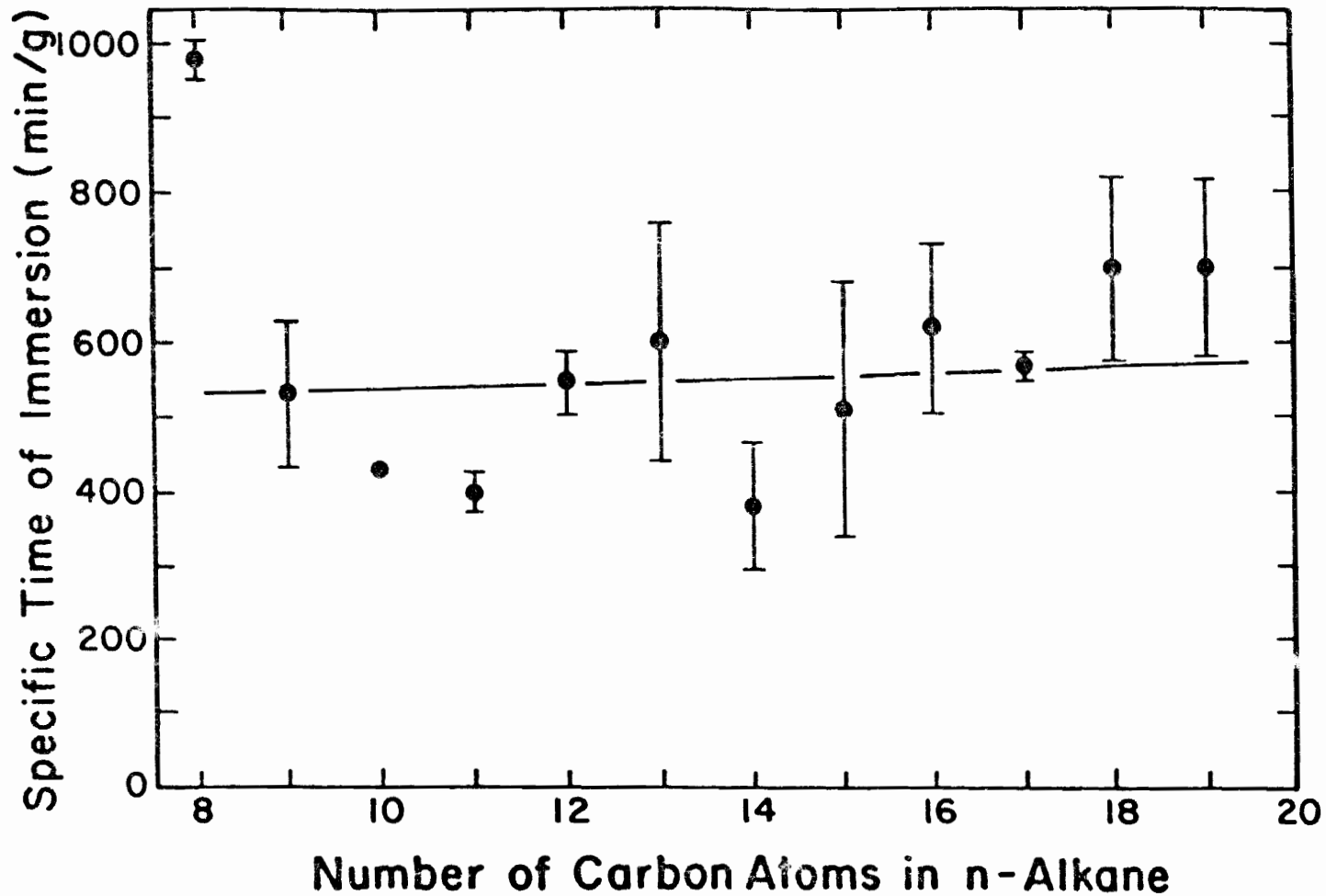


Figure 12. Time of Immersion of Pocahontas No. 3 coal in n-alkanes versus carbon number of the n-alkane.

surprising result since the specific immersion time was found (51) to be sensitive to n-alkanol chain length, displaying a maximum for n-butanol. There is no clear maximum or minimum in the results shown in Figure 12. However, again in the range of similar chain length (C8-C12), the specific immersion times are comparable (500-800 min/g for n-alkanols and 400-1000 min/g for n-alkanols). This suggests again that the hydroxyl functionality plays little or no role in determining the immersional behavior of coal in n-alkanols.

The immersion time for octane is noticeably longer than for the remainder of the alkanes. Since the heat of immersion was highest in octane, this wetting liquid must be accessing more surface than the longer alkanes. The specific immersion time then reveals the slow penetration of octane into pores not accessible to nonane, for example. The time of immersion, together with the heat of immersion, yields information about reagent accessibility to coal surfaces.

B. Immersion in Cyclic and Heterocyclic Hydrocarbons

Table V lists the heats and times of immersion for Pocahontas No. 3 coal in several cyclic hydrocarbons, three of which contain nitrogen. The first two, tetralin and 1-

TABLE V

HEATS AND TIMES OF IMMERSION FOR POCAHONTAS NO. 3 COAL
IN CYCLIC AND HETEROCYCLIC HYDROCARBONS

Immersion

<u>Liquid</u>	<u>H_{imm}</u>	<u>T_{imm}</u>
Tetralin	6.6 ± 0.1 J/g	590 min/g
1-methyl naphthalene	7.6 ± 0.1 J/g	660 min/g
Quinoline	6.9 ± 0.7 J/g	1800 min/g
Tetrahydro- quinoline	8.1 ± 0.7 J/g	840 min/g
Pyridine	12.8 ± 0.5 J/g	1400 min/g

methylnaphthalene and pure hydrocarbons. Tetralin, or 1,2,3,4-tetrahydronaphthalene, consists of one saturated and one unsaturated six-membered ring. 1-Methyl naphthalene consists of two unsaturated rings with a methyl group attached to carbon 1. The heat of immersion in 1-methylnaphthalene, 7.6 J/g, is only slightly higher than the heat of immersion in tetralin, 6.6 J/g. Since coal is primarily hydrocarbon in nature, the interaction of both of these liquids with the coal surface should be non-specific. Thus, the higher heat of immersion for 1-methylnaphthalene indicates that this molecule can access more surface area than tetralin. The fact that 1-methylnaphthalene is largely planar, with the exception of the methyl group, explains the ability of this molecule to access more of the coal surface. Tetralin, on the other hand, contains a saturated ring which is not a planar structure.

The times of immersion of Pocahontas No. 3 coal in tetralin and 1-methylnaphthalene, however, indicate that the two molecules negotiate the porous network of coal with a similar degree of difficulty. The specific immersion time in tetralin was only slightly shorter than the specific immersion time in 1-methylnaphthalene, 590 min/g in tetralin compared to 660 min/g in 1-methylnaphthalene. The difference between the two values is probably insignificant

since time of immersion measurements often vary by more than 10%.

The remaining liquids in Table V are nitrogen-containing cyclic hydrocarbons. Pyridine is the only single-ring molecule in this group and displays the highest heat of immersion. Pyridine is known to interact specifically with coal macromolecules causing swelling (10,21). Thus, the expansion of the coal structure upon swelling allows pyridine to access more surface area, resulting in a higher heat of immersion over the case of a non-swelling adsorbate, for example, 1-methylnaphthalene.

The heats of immersion of Pocahontas No. 3 coal in quinoline and tetrahydroquinoline are 6.9 and 8.1 J/g, respectively. While the difference between these two values seems significant, an examination of the error associated with each value reveals no real difference. In general, the errors encountered with heterocyclic liquids are much larger than the errors associated with pure hydrocarbons.

A comparison of the immersional behavior of tetrahydroquinoline and tetralin affords an opportunity to examine the effect of nitrogen inclusion into a ring. The heat of immersion of coal in tetrahydroquinoline is 8.1 J/g compared to 6.6 J/g for tetralin (tetrahydronaphthalene). Since the two molecules are the same size, any difference in

the heat of immersion must be due to a difference in the type of interaction between the adsorbate and the surface or due to a greater available surface area as the result of swelling. In this case, both liquids are known to swell coal slightly (10). Tetrahydroquinoline, however, has a greater chance to hydrogen bond to coal due to the presence of nitrogen in the saturated ring and swells coal more than tetralin. Thus, the combination of greater available surface area and stronger hydrogen bonding in the case of tetrahydroquinoline results in a higher heat of immersion.

In general, one notes that the times of immersion of coal in heterocyclic hydrocarbons are longer than in cyclic hydrocarbons. The heat of immersion is governed by the size of bulk of the adsorbate and the ability of the adsorbate to hydrogen bond to coal. Thus, cyclic hydrocarbons exhibit lower heats and shorter times of immersion than their heterocyclic analogs.

C. Immersion of Unextracted and Extracted Pocahontas No. 3 Coal

Table VI shows the heats and times of immersion of Pocahontas No. 3 coal in methanol and pyridine. Also shown are the heats and times of immersion of the coal in methanol and pyridine following extraction with either methanol or

TABLE VI

HEATS AND TIMES OF IMMERSION FOR
EXTRACTED AND UNEXTRACTED POCAHONTAS NO. 3 COAL
IN METHANOL AND PYRIDINE

Immersion	Extraction		
<u>Liquid</u>	<u>Solvent</u>	<u>Himm</u>	<u>Timm</u>
Methanol	None	23.3 ± 1.6 J/g	564 ± 30 min/g
Methanol	Methanol	23.7 ± 1.2 J/g	614 ± 23 min/g
Methanol	Pyridine	21.0 ± 1.1 J/g	572 ± 36 min/g
Pyridine	None	12.1 ± 0.3 J/g	1449 ± 28 min/g
Pyridine	Pyridine	14.4 ± 0.5 J/g	2013 ± 169 min/g

pyridine.

All three coals, the unextracted coal, the methanol extracted coal, and the pyridine extracted coal, exhibit the same heat of immersion in methanol. Apparently, prior extraction with methanol or pyridine does not alter the amount of surface area available to methanol. Furthermore, the time of immersion in methanol is similar for all three coals. Thus, prior extraction with methanol or pyridine does not influence the ease with which methanol can access the available surface of coal.

However, the heat and time of immersion of coal in pyridine, as shown in Table VI, is increased by prior extraction with pyridine. The heat of immersion of the pyridine extracted coal in pyridine is about 20% higher than the unextracted case. This result is not entirely surprising and is due to the fact that pyridine interacts specifically with the macromolecular structure of coal (21). Larsen and Lee (55) note that the removal of pyridine solubles from coal increases both the surface area of coal and the amount by which coal is swollen. Clearly, if pyridine extraction increases the surface area of coal, subsequent heat of immersion values should be greater. Also if pyridine extracted coals swell to a greater extent than unextracted coals, more surface area would be accessible to

the adsorbate in the former case.

Likewise, prior extraction with pyridine increased the time of immersion of Pocahontas No. 3 in pyridine. Through pyridine extraction increases the degree of swelling of coal, solvent swelling may take several hours to reach equilibrium (55). Thus, previously extracted coals may give higher heats of immersion in pyridine than unextracted coals due to increased swelling over the unextracted case. However, the added surface area due to swelling may not be available until a "swelling equilibrium" has been established.

Pyridine extracted coal immersed in methanol, however, does not show an increase in the heat of immersion over the unextracted case as noted above. The difference in the behavior of the pyridine extracted coal in methanol and in pyridine is due to the fact that methanol swells coal only slightly and extracts less than 1 weight percent of coal (56). Even though the pyridine soluble portion of a coal sample was extracted, subsequent immersion in methanol showed no increase over the unextracted case. This indicates that the ability of pyridine to swell coal accounts for the increased heat of immersion in pyridine for the pyridine extracted case over the unextracted case.

D. Immersion of Oxidized Pocahontas No. 3 Coal

1. Heat of Immersion

The effect of oxidation time at 320°C on the heat of immersion of unextracted and extracted Pocahontas No. 3 coal in water is shown in Figure 13. The heat of immersion in water increases rapidly with oxidation time at 320°C for all coal samples and approaches a maximum value after about 5 hours of oxidation. The heat liberated by a sample oxidized for 18 hours is almost 30 times as great as the heat of immersion of the unoxidized coal. The result is consistent with the findings of Phillips et al. (36), who report a fifty-fold increase in the heat of immersion of a Virginia coal heated to 320°C for 24 hours over the unheated coal.

Prior extraction of the coal with either methanol or pyridine had no effect on the heat of immersion in water before or after oxidation. As Figure 13 illustrates, the heat of immersion of the unoxidized coals in water was identical. After only one hour of oxidation, the heat of immersion of all three coals increased twenty-fold. The heat of immersion in water is sensitive to the presence of surface bound oxygen on coal (36) and can be used as a relative measure of the oxidation process. Since the heat of immersion in water was unaffected by prior extraction with methanol or pyridine, then surface oxidation must occur

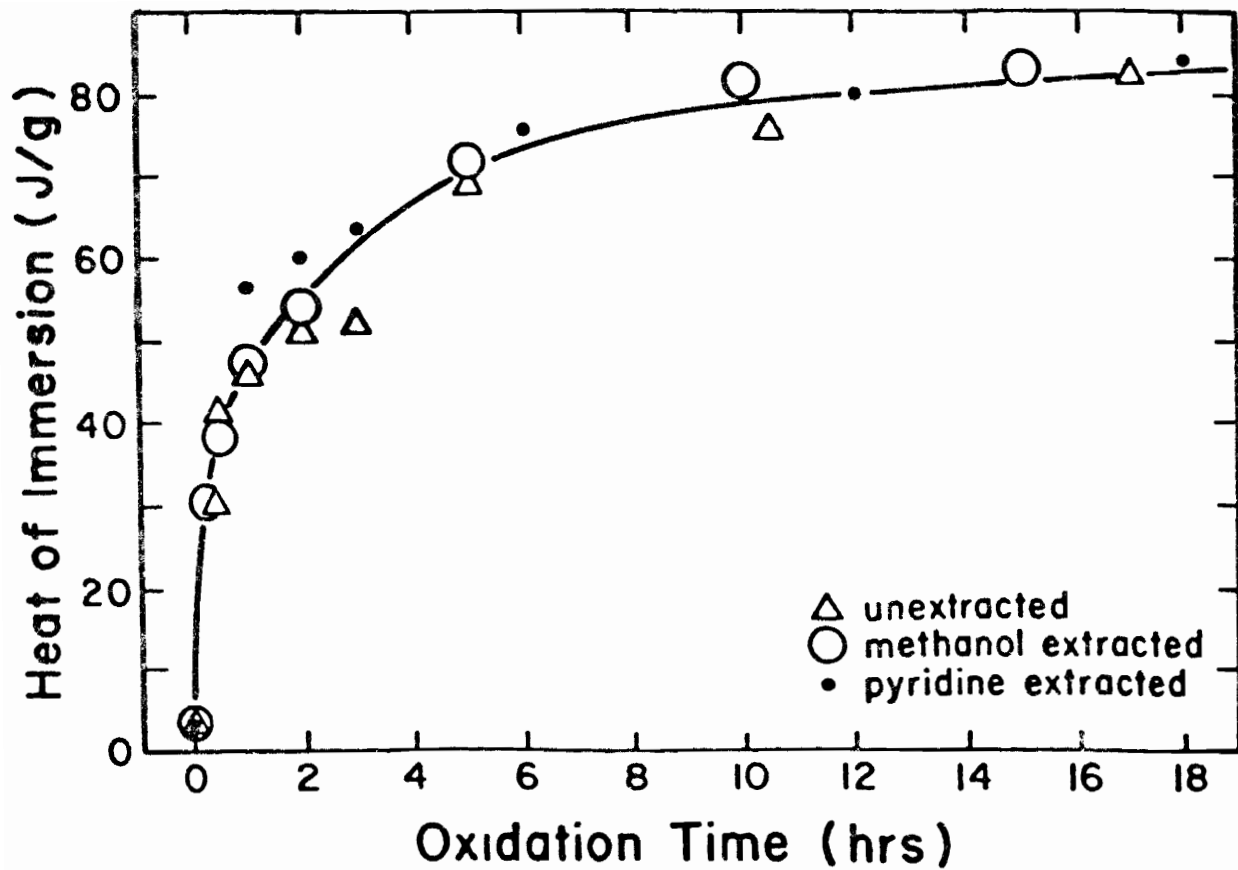


Figure 13. Heat of immersion of Pocahontas No. 3 coal in water versus oxidation time at 320°C.

similarly in both unextracted and extracted coal. More specifically, at any point in the oxidation process, the amount of oxidized surface area on the unextracted coal is the same as that of either extracted coal. Clearly, the oxidation of coal, and subsequent immersional measurements in water, are unaffected by previous extraction with methanol or pyridine.

2. Time of Immersion

The specific times of immersion for the unextracted coal and the two extracted coals as a function of oxidation time are shown in Figure 14. For all three coals the specific immersion time in water increases markedly within the first five hours of oxidation. After five hours, the specific immersion time of the unextracted coal continues to rise nonlinearly. The specific immersion time for the methanol and pyridine extracted coals, on the other hand, levels off around 7000 min/g and shows no further increase with oxidation time at 320°C.

The specific immersion time is a measure of the ease or difficulty with which the adsorbate molecule can access the available surface of coal. Furthermore, the oxidation of coal is known to progress from the external surface inward (25). After five hours of oxidation, the heat of immersion

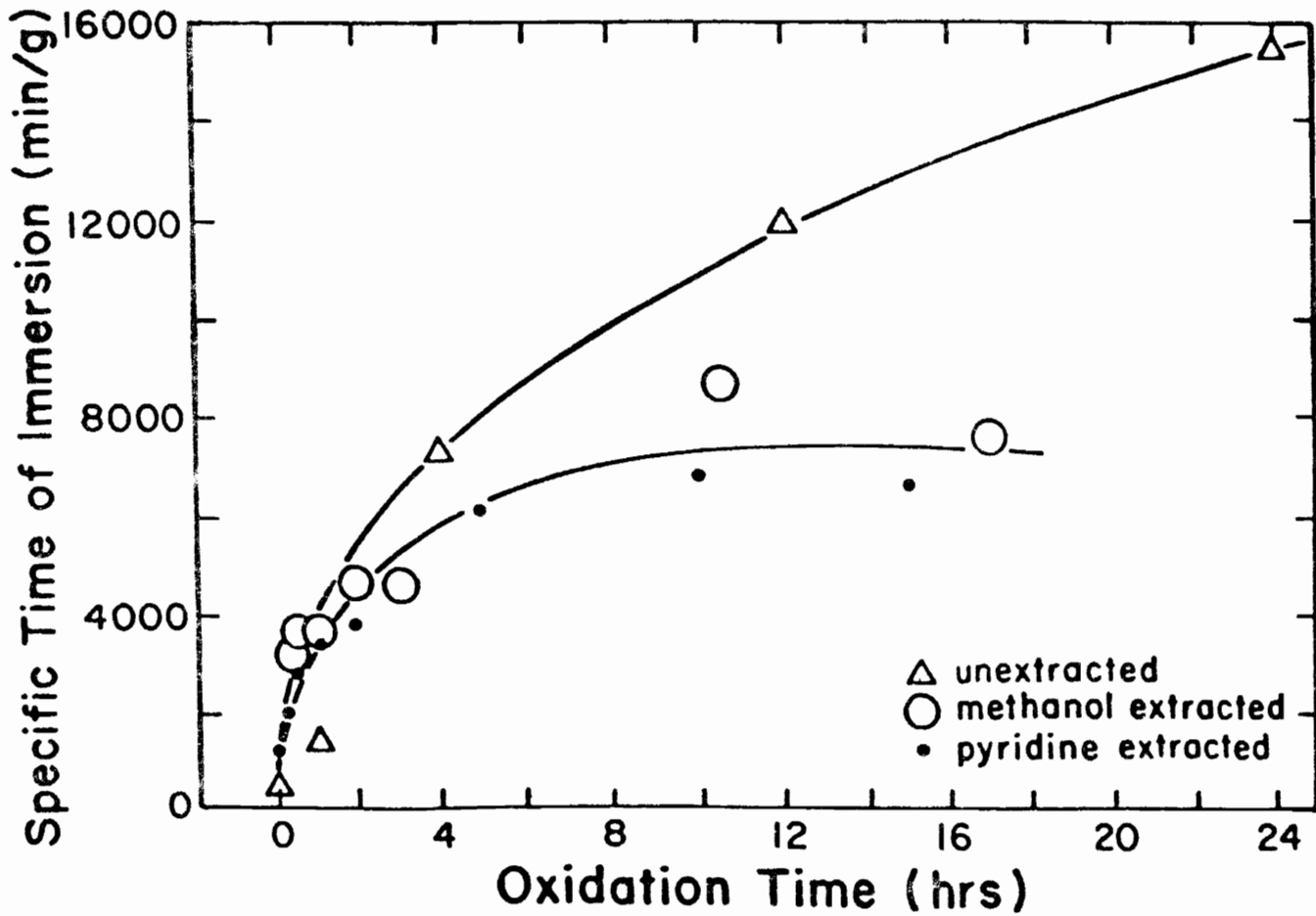


Figure 14. Time of immersion of Pocahontas No. 3 coal in water versus oxidation time at 320°C.

(and the amount of newly oxidized surface) increases only slightly (see Figure 13). However, the time required for water to access and wet this surface continues to increase for the unextracted coal. The continued rise in specific immersion time is explained by the presence of oxidized surface in regions of the coal pores which even water has trouble accessing.

Contrary to the unextracted coal, the methanol and pyridine extracted coals attain a maximum in the specific immersion time in water after 5 hours of oxidation. This behavior more closely follows the trend found for heat of immersion (see Figure 13). Apparently, the newly oxidized surface formed after sixteen hours of oxidation is as accessible to water as that formed after only five hours of oxidation. Solvent extraction, then, has made the oxidized surface more accessible to water.

The rationale which explains this difference in behavior between extracted and unextracted coal is as follows: some of the oxidized surface of the unextracted coal lies within narrow pores which are partially blocked by potentially soluble molecules adsorbed on the pore walls (17). These molecules do not hinder the approach of oxygen, thus oxidation occurs in these narrow pores. However, these molecules do restrict the approach of water and lengthen the

time of immersion in water. In the case of the extracted coals, all or some of these potentially soluble molecules are removed. Some of the oxidized surface of the extracted coals lies within narrow pores, but the pores are not blocked by adsorbed molecules.

E. X-ray Photoelectron Spectroscopy of Oxidized Pocahontas No. 3 Coal

Figure 15 shows the effect of oxidation time at 320°C on the oxygen-carbon ratios obtained by x-ray photoelectron spectroscopy of the three coals. X-ray photoelectron spectroscopy (XPS) is a surface sensitive analytical technique which gleans chemical information from the top 5-10 nm of a solid surface. Therefore, the ratios given in Figure 15 are surface oxygen-carbon ratios.

The XPS oxygen-carbon ratios of the unextracted, the methanol extracted and the pyridine extracted coal increase rapidly with only a few hours of oxidation. The oxygen-carbon ratio of the two extracted coals approaches a value of 0.55 as oxidation continues. The oxygen-carbon ratio of the unextracted coal, however, levels off to a lower value around 0.45. This apparent discrepancy is best explained by the fact that the XPS results were calculated from single determinations on the various coal samples. The XPS oxygen-

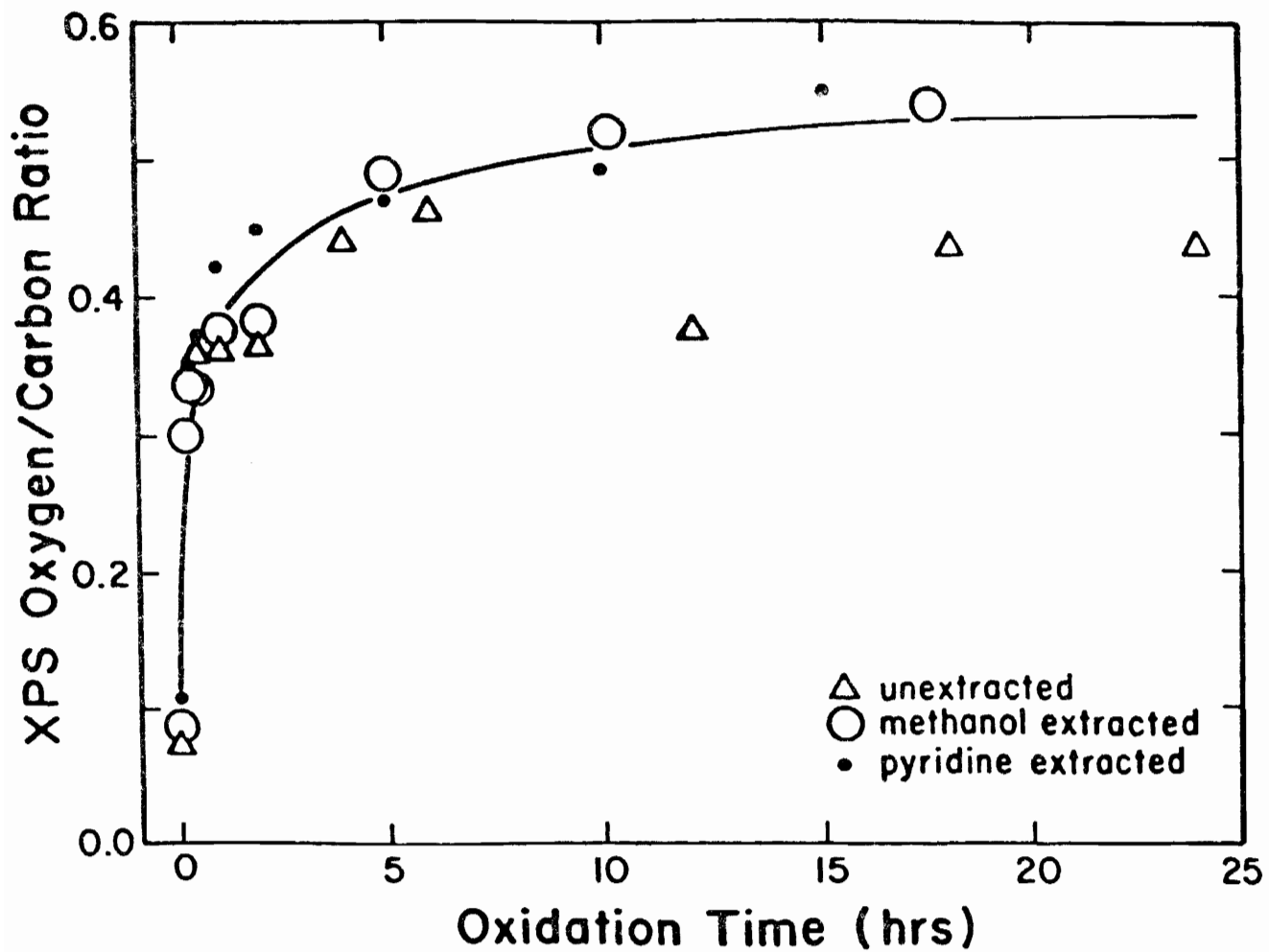


Figure 15. XPS oxygen/carbon ratios of Pocahontas No. 3 coal versus oxidation time at 320°C.

carbon ratios then are not average or mean values. Despite this shortcoming, the results in Figure 15 display a distinct trend which accentuates the rapid inclusion of oxygen on the surface of all three coals. This trend is very similar to that found for the heat of immersion as a function of oxidation time (see Figure 13).

A useful characteristic of XPS is the ability to resolve a composite spectra into individual photopeaks. An example of this curve-fitting is shown in Figure 16. In this case, the carbon 1s spectra of the methanol extracted coal has been resolved to reveal the contribution of carbon-oxygen photopeaks to the overall composite spectra. The unoxidized coal spectra ($t=0$ hours) includes contributions from C-C, C-O and even C=O surface species. As oxidation progresses, three types of carbon bound to oxygen are prominent: C-O, C=O, and O-C-O. The chemical shifts for these three species from C-C centered at 285 eV are, respectively, 1.3, 2.6 and 4.2 eV. The identification of these surface species on coal during oxidation supports models of oxidation such as that shown in Figure 5.

The XPS oxygen-carbon ratios and the heats of immersion show a similar dependence to oxidation time at 320°C. Therefore, the heat of immersion versus the XPS oxygen-carbon ratios of the two oxidized, extracted coals is

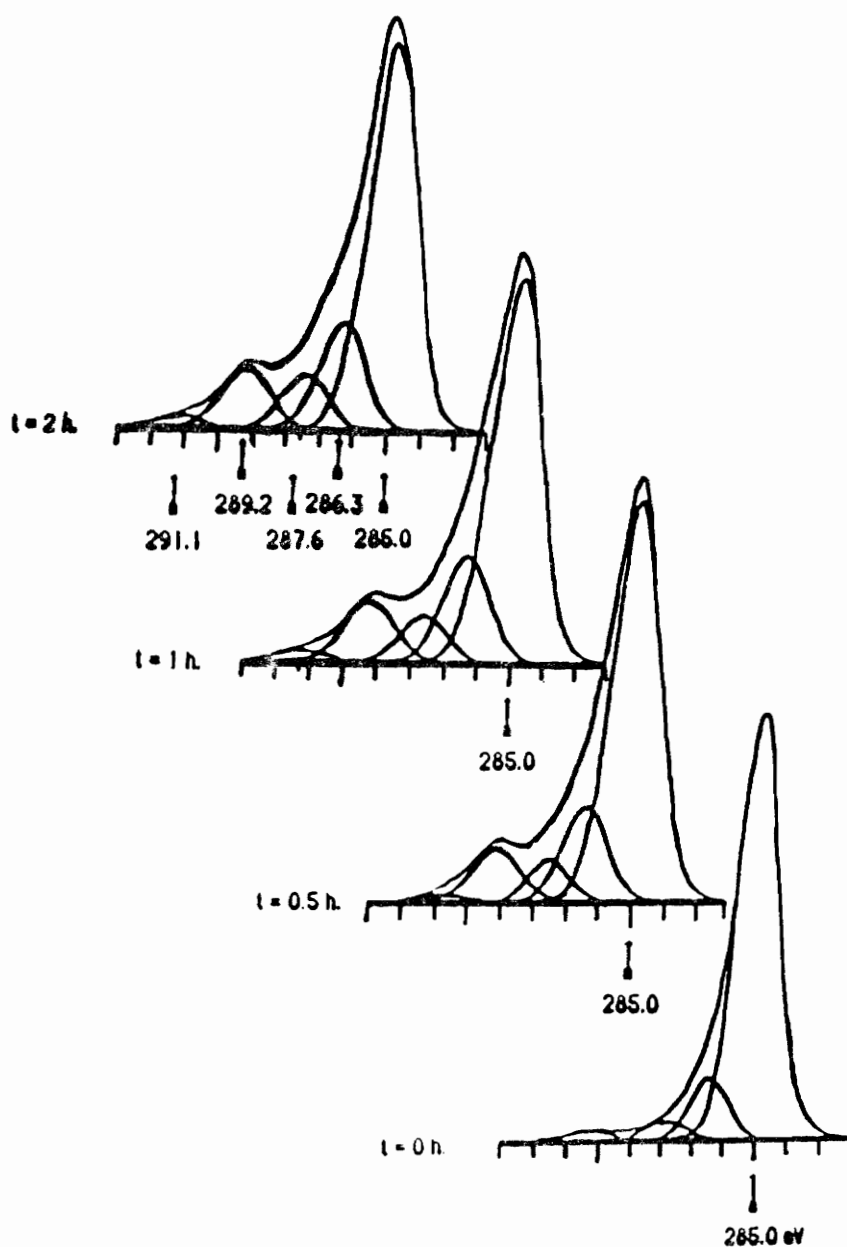


Figure 16. Curve-fitted photopeaks for the carbon 1s spectra of methanol extracted Pocahontas No. 3 coal following oxidation at 320°C.

plotted in Figure 17. A linear correlation is noted between heat of immersion and the XPS oxygen-carbon ratios for the extracted coals. No correlation was found for the heats of immersion and XPS oxygen-carbon ratios of the unextracted coal. Correlation between heat of immersion and XPS results have been reported only once before. Phillips et al. (36) found a similar correlation between the heats of immersion in water and the XPS oxygen carbon ratio of a Virginia coal heated to various temperatures for 24 hours. However, this is the first reported study of the oxidation of coal as a function of time at one particular temperature using both microcalorimetry and XPS.

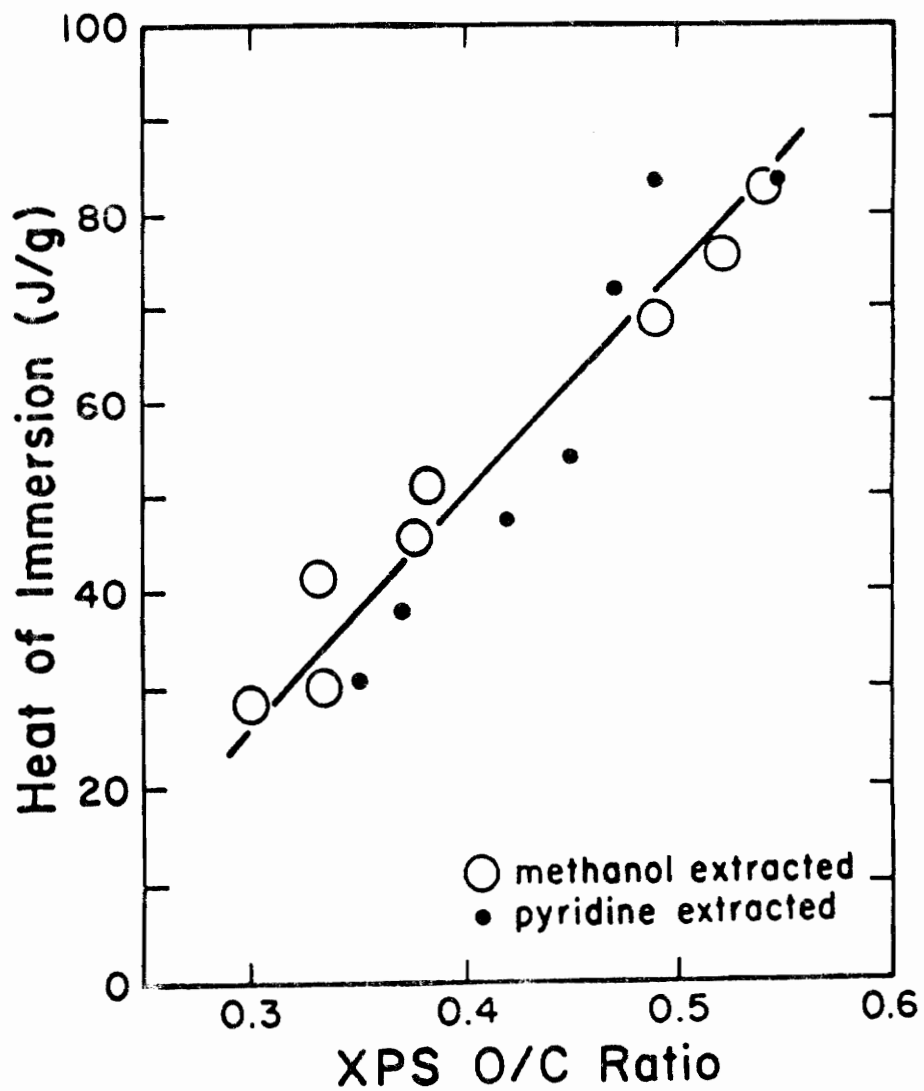


Figure 17. Heat of immersion in water versus XPS oxygen/carbon ratios of extracted Pocahontas No. 3 coal.

Chapter V

SUMMARY

The immersional behavior of Pocahontas No. 3 coal was examined in a variety of systems. The systems involved comparing differences in the wetting liquids used or varying the surface of coal by extraction or oxidation or both extraction and oxidation. The results are summarized below.

The immersion of coal in a homologous series of n-alkanes reveals information about liquid penetration of coal particles. The heat of immersion of coal decreased nonlinearly as alkane chain length increased, and leveled off after tridecane. However, the heat of immersion displayed a more linear relationship to the molarity of the n-alkane, which is a better measure of overall molecular size than chain length. The time of immersion was found to be longest for n-octane. This reveals the slow penetration of octane into pores not accessible to n-nonane, for example.

The immersion of coal in cyclic and heterocyclic hydrocarbons revealed two trends. In general, the times of immersion in heterocyclic hydrocarbons was longer than in non-nitrogen containing hydrocarbons. The heat of immersion was governed by the size of bulk of the liquid molecule and

the ability of the molecule to hydrogen bond to coal. Thus, cyclic hydrocarbons exhibit lower heats and shorter times of immersion than their heterocyclic analogs.

Prior extraction of coal with methanol produced no change in heat of time of immersion values in methanol and pyridine over the unextracted case. Extraction with pyridine increased the heat and time of immersion in pyridine due to the removal of pyridine-soluble coal molecules. The presence of these molecules hinders the ability of pyridine to swell coal and thereby wet more surface area.

The effect of air oxidation of the coal was to rapidly increase the heat of immersion in water for both extracted and unextracted coal. Thus, immersion in water revealed the increased oxygen content of the surface. Prior extraction with either methanol or pyridine had no effect on subsequent oxidation or on the heat of immersion in water. The removal of a portion of coal molecules soluble in both methanol and pyridine shortened the times of immersion in water.

XPS spectra of the oxidized coals revealed a rapid increase in the surface oxygen-carbon ratio with oxidation time at 320°C. Curve-fitting of the carbon 1s spectra revealed the presence of at least 3 carbon-oxygen species on oxidized coal, namely, C-O, C=O, and O-C=O. The heats of

immersion in water displayed a linear correlation with XPS O/C ratios for the two extracted coals. Thus, a thermodynamic and spectroscopic technique yielded complementary information regarding the oxidation of coal.

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