Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Kwon, K. C. , Finseth, D. H. and Lai, R. W.(1990) 'Study on Surface Properties of Coal, Using Various Probe Compounds', Separation Science and Technology, 25: 13, 1871 — 1892
To link to this Article: DOI: 10.1080/01496399008050430
URL: http://dx.doi.org/10.1080/01496399008050430

SEPARATION SCIENCE AND TECHNOLOGY, 25(13-15), pp. 1871-1892 (1990)

STUDY ON SURFACE PROPERTIES OF COAL, USING VARIOUS PROBE COMPOUNDS

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ABSTRACT

Pittsburgh seam coal, Wyodak coal and Illinois #6 coal were treated by heating, steaming and oxidizing them in order to modify surface properties of the coals at 150-220°C and atmospheric pressure, and compare adsorption responses of probe compounds, using a high pressure liquid chromatograph (HPLC). Probe compounds include toluene, Isopropanol, heptanol and phenol. Adsorption of xanthates on 120 mesh Rico Colorado pyrite was investigated at 25°C, using the inverse chromatographic technique. The concentration range of xanthates in pH 3.9 aqueous solution is 0.1-1 g/kg-solution. Xanthates include potassium amyl xanthate, sodium isopropyl xanthate and sodium ethyl xanthate for this investigation.

INTRODUCTION

Coal is the most plentiful energy resource in the United States and continues to be the major fuel utilized by electrical power plants. The coal resources will become more attractive for chemical feedstocks as well as sources of liquid and gaseous fuels, as petroleum resources become more depleted.

Current annual coal production averages about 700-800 million tons in the United States and 3.3 billion tons for the entire world. Reserves of coal are far greater than the known reserves of all other mineral fuels (petroleum, natural gas, oil shale, and tar sands) combined (1). Electric utility companies consumed 550 million tons of coal in 1985, whereas coke production industry used 67 million tons of coal in 1980 (2).

Coal is a very complex and heterogeneous material. Effective utilization of coal requires an understanding of the formation, structure, and purification of coal. Raw coal consists of minerals and organic matter. Coal minerals include primarily pyrites, silicates (clays) and various minor minerals, whereas organic matter is composed of carbon, oxygen, hydrogen, nitrogen and sulfur.

Extensive research on physical and chemical coal cleaning is being carried out to increase a heating value of coal and reduce pollution of the environment by sulfur oxides, nitrogen oxides and toxic metals, produced during the combustion of coal. Physical coal cleaning is a method for upgrading raw coal by removing physically undesired mineral impurities. Physical coal cleaning methods are mainly classified into three categories: gravity, flotation and agglomeration.

Sulfur in coal is present as organic sulfur, pyritic sulfur and sulfate sulfur. Sulfur occuring in the form of relative coarse pyrite particles is removed largely by density separation, but very finely disseminated pyrite and organic sulfur cannot be removed in this way. Sulfur products in combustion not only pollute the environment, but also are detrimental to combustion systems because of the corrosive action of their combustion products. Sulfur is a harmful impurity in all metallurgical products. Therefore, high-sulfur coal is unsuited for smelting or heat-treating processes, where products of combustion come into direct contact with the material under treatment (3).

The ash-forming impurities in coal not only dilute the combustible contents of the coal and thus decrease its heating value, but also reduce the effective capacity of the burning equipment. Minerals cause solid build-up and corrosion on boiler surfaces, due principally to alkali metals and alkali chlorides from clay minerals.

The flotation process does not separate on the basis of specific gravity but rather depends upon wettability difference between the surface of coal and those of coal mineral impurities, using water as a liquid media. Various additives such as surfactants (4), frothing agents and depressants are employed to increase wettability difference between the surface of coal and those of mineral impurities, and decrease the surface tension of water. The surface of coal is less hydrophilic than those of coal mineral impurities such as pyrites and silicates. Coal particles selectively attach themselves to the bubbles of a froth formed with a frothing agent and air, and are buoyed to the interface between the water and air, where they may be removed. The mineral impurity particles wetted by the water do not attach to the bubbles and remain below the water surface, and can thus be separated from the coal (5).

The chief advantage of the flotation process is the fact that it is suited to cleaning coal of the finer sizes which cannot be treated as effectively by the other cleaning processes. The second advantage of the flotation process is that the hydrophobicity of various compounds on the coal surface can be controlled by treating the coal surface with chosen chemicals.

The surface polarity increases with the concentration of the functional groups such as phenolic hydroxyl and carboxyl. The higher concentration of the polar surface functional groups decreases hydrophobicity of the coal, resulting in less coal flotability. Heats of adsorption of water on coal decrease with increased coal hydrophobicity (6).

The presence of phenolic hydroxyl groups, and especially of carboxylic acid group, is highly dependent on the coal content. Coal flotability is at a maximum with coals containing about 92 w % carbon and decreases with both decreasing and increasing carbon content (7).

In oil agglomeration method, the carbonaceous fraction of coal can be agglomerated and recovered from aqueous suspension with many different oils as collecting liquids. Inorganic or ash-forming coal minerals do not agglomerate and remain in suspension to be rejected. There appears to be virtually no lower limit on the particle size suitable for oil agglomeration (8).

General difficulties have been experienced in removing pyrite by surface wetting differentiation method such as froth flotation and oil aggromeration. Many researchers have recently focused on chemical alteration of the pyrite surface with chemical compounds such as aqueous ferric sulfate solution and a warm alkaline solution containing dissolved oxygen. Consideration has also given to the chemical or physical treatements of coal by alcohols, steam and thermal heating, before it is subjected to froth flotation.

Several methods of studying adsorption of additives such as surfactants and other chemicals at solid-liquid interfaces have been employed. These include adsorption isotherms, electrokinetics data, and contact angle measurements. Recently, many researchers utilize calorimeters to measure heat of interaction at the liquid-solid interfaces. More recently, the inverse gas chromatography technique was employed to analyze surface properties of various coals, using probe gaseous compounds as adsorbates. These methods appear to be time-consuming, tedious and difficult to be utilized for the systematic study on changes in surface properties of raw and treated coals. A convenient and sensitive method, the so-called inverse liquid chromatography technique, was applied to evaluating surface properties of raw coals and various treated coals for fine coal benefication in this study.

PREVIOUS WORK

All coal cleaning processes in general use are gravity-concentration methods. Methods based upon surface properties are employed for the futher benification of fine coals in order to clean coal acceptable to the strict air pollution regulations. The froth flotation process depends on hydrophobicity differences between the surface of coal and those of its coal mineral impurities, using water as a liquid media. The froth flotation process is independent of specific gravity, and depends almost completely on the surface properties of the coal.

Coal flotability is dependent on the oxidation state of the coal, the surface polarity and the coal rank. The significant oxygen-containing functional groups in coal are carbonyl, hydroxyl, carboxylic acid, and methoxyl (9). The high concentration of surface polar groups results in a reduced surface hydrophobicity and hence a lessened flotability during the flotation experiments. Coal is an extremely reactive material toward oxidation. Even small amounts of air (oxygen) can significantly alter the physical and chemical properties of a coal (10). Oxidation of the coal surface results in an adverse effect on its flotability (11). An oxidized coal tends to be more hydrophilic.

Research on chemical and physical technology is needed for understanding variables involved in enhancing wettability differences between the surface of coal and those of its impurities in fine coal preparation processes.

Coal is treated chemically to reduce the concentration of the polar functional groups through the etherization and esterification of coal surface functional groups with methanol and an acid catalyst to increase hydrophobicity of coal (12). In the esterification of organic acids with alcohols, the rate and extent of esterification depend upon the structure of the molecules involved and types of radicals present. With acetic acid as a catalyst at 155°C, the primary alcohols are esterified most rapidly and completely. The secondary alcohols react much slower and have lower limits of esterification (13).

Coals are heated at elevated temperatures to reduce hydrophilic functional groups on coal surface by removing some volatile matter. Coals are also treated with high pressure steam to leach out some polar compounds from coal surface (10).

Many researchers are interested in the alteration of pyrite surface through chemical reaction in order to improve separation of coal and pyrites. When ground coal was pretreated with a warm alkaline solution containing dissolved oxygen and subsequently separated by either oil agglomeration or froth flotation, significantly more sulfur was removed in comparison of either oil agglomeration or froth flotation alone (14).

The relative hydrophobicity of a given coal can be evaluated by measuring coal flotability, and heats of immersion of coal into water. The coals of various ranks and the solid minerals associated with coal were characterized in terms of relative hydrophobicity through the values of heat of immersions of coals in water and in methanol, using a Setaram C-80 flow microcalorimeter. Heats of immersion of coal were also measured in surfactant solutions of varying concentrations. Heats of immersion of coal were found to correlate well with coal flotability (6).

Numerous investigators (15,16) employed the inverse chromatography technique to study surface properties of polymers, Chromosorbs, Porapak Q, and chemically treated compounds such as silicas and asphalts, using probe compounds. More recently, several researchers attempted to utilize this technique in the study of surface properties of coal such as reactivity, surface energy, polarity, softening point and penetration of probe compounds into the coal structure.

The inverse chromatography technique was initially used for the study of polymer properties. The polymer was used as the stationary phase in the study on the interaction between the polymer and volatile solutes. Inverse chromatography is based on the distribution of a probe compound between a mobile phase and a stationary solid phase. The probe compound is introduced at the column inlet and is swept through the column by the carrier fluid. The distribution coefficient is dependent on the volumetric flow rate of the carrier fluid, the amount of the solid packing material and the mass of the probe compound introduced into the column (15).

In the inverse gas chromatography technique, the surface properties of the column packing as the analyte are charaterized by the retention behavior of solute probes. Energy distribution functions of chloroform-adsorbed alumina and graphitized carbon black, and diethyl-ether-adsorbed unsilanized and silanized silica were evaluated directly from chromatographic retention volumes (16).

A rapid method of determining relative polarity of surfactants was developed by comparing the retention times of methonol and n-hydrocarbons in a liquid-phase surfactant packed column. Relative polarity values are found to be related to the hydrophile-lipophile properties of the probe compounds tested. A greater proportion of free hydroxyl groups increases the polarity of surfactants (17).

The surface properties of silicas modified with alcohols were investigated with probe compounds by inverse gas chromatography. The surface properties such as standard free energies of adsorption, surface energies and enthalpies of adsorption were determined with retention volumes from inverse chromatography at various temperatures. The probe chemicals include alcohols such as methanol, ethanol and butanol, alkanes with the carbon number 6 through 10, ether, chloroform and benzene (18,19).

The use of peak broading studies in gas chromatography is known to be a useful means of obtaining information about both the physical and chemical nature of polymeric adsorbents. The porous structures of several available adsorbents such as Chromosorbs and Porapak Q were examined with variety of molecular probes such as chloroform, benzene, cyclohexane, and hexane. Relative peak broading for benzene and chloroform on Porapak Q was observed to increase with increased temperature. This behavior probably indicates greater penetration of these vapors into the amorphorous polymer in addition to deeper penetration into relatively small pores (20).

Asphalts were reacted with N,O-bis (trimethylsilyl)acetamide (BSA) and hexamethyldisilazane (HMDS) at 160°C. Silylation of asphalts within inverse gas-liquid chromatographic columns offers a convenient means to study asphalt functional groups such as phenolic and carboxylic acid OH functional groups, using probe compounds such as phenol and propionic acid. Asphalt contains many types of functional groups that were found to exhibit selective affinities for specific probe compounds by calculating specific interaction coefficients with retention volume data of probes from inverse chromatography (21). In the same way, surface properties of coal can be successfully evaluated by choosing proper probe compounds and proper operation conditions of a chromatograph.

The properties of lignites were studied by a molecular probe technique, using probe compounds such as air, carbon dioxide, water, methanol and hexane. The probe molecules are adsorbed on the surface of lignite by adsorption mechanism alone up to 175°C, irrespective of their chemical identity. Water and methanol adsorbed on active hydrophilic sites in monolayer or submonolayer coverage can only be eluted easily around 175°C. The column permeability appears to depend on the sulfur content of lignites (22).

An Illinois No. 2 hvb coal was used as a packing material for an inverse gas chromatographic column, using methane as a probe compound. The column temperature was gradually increased to identify the glass transition temperature for the coal. An Upper Freeport medium volatile bituminous coal was packed as a packing material for an inverse liquid chromatographic column. The probe compounds included benzene, naphthalene, phenanthrene, and triphenylene at 27-80°C to compare affinities of aromatic compounds with different aromatic ring sizes and obtain heats of interaction of the probe compounds on the coal (23,24).

A 28 x 0 mesh, Illinois No. 6 high-volatile bituminous coal was packed as a packing material in an inverse gas chromatographic column. The probe compounds include methane, pentane, hexane, cyclohexane, benzene, methanol, propanol, pyridine, 2,4-dimethylphenol, and o-ethylphenol to study the changes in coal reactivity as a function of various pretreatments. No major shift in methane's retention time or change in peak shape occured until after the column temperature was raised above 215°C. At higher temperatures, the methane retention times increased and the peak shapes broadened. This observation may be due to irreversible changes in the coal structure (23).

EXPERIMENTAL RESULTS AND DISCUSSION

Pittsburgh seam coal, Wyodak coal and Illinois #6 coal were treated to investigate changes in their surface properties favorable to the removal of their impurities. Changes in surface properties of the coals were analyzed, using several selected probe compounds via a high pressure liquid chromatograph (HPLC) in this study. Toluene was chosen as a representative of aromatic compounds. Isopropanol and heptanol were selected as polar compounds, whereas phenol was chosen as an aromatic acid compound. Wyodak coal is selected as a representative of subbituminous coal, Illinois #6 coal as a representative of high volatile bituminous coal and Pittsburgh seam coal as a representative of high-rank bituminous coal.

The coals were heated under nitrogen atmosphere to remove hydrated surface water and some labile compounds. The coals were steamed to eliminate some hydrophilic compounds on the coal surface and clean out the coal surface. The coals were also

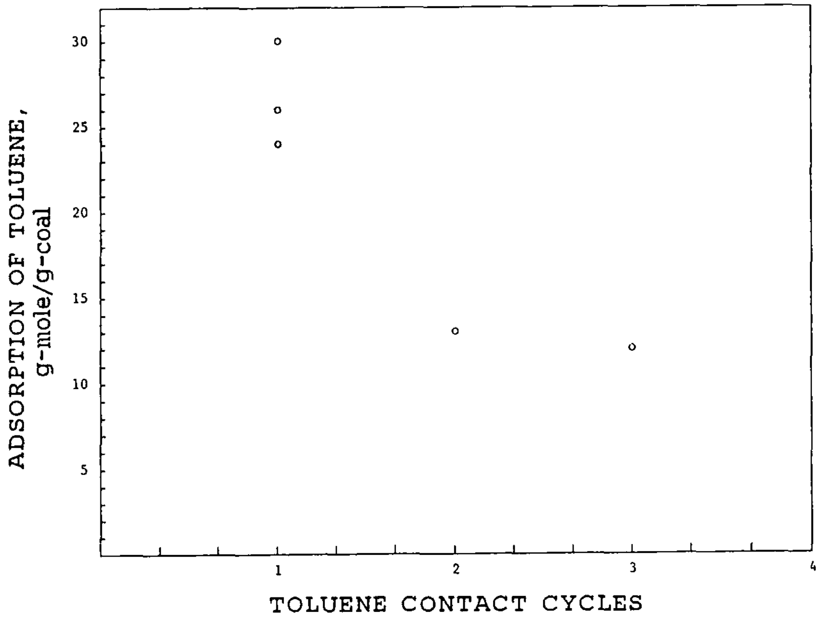

Figure 1. Adsorption of toluene on 100-140 mesh untreated Pittsburgh coal in 0.01341 w % aqueous solution at 32°C.

oxidized with dry air to oxidize some labile compounds and minerals on the coal surface.

Adsorption of toluene on Pittsburgh coal is examined in 0.0134 w % aqueous solution at 32°C. The adsorption range of toluene on Pittsburgh coal is 24-30x10^{-6} g-mole/g-coal, when the coal is soaked for the first time in toluene aqueous solution. The same toluene-soaked coal is washed with water and then is soaked again in the toluene aqueous solution to evaluate adsorption of toluene on the coal. Adsorption of toluene on the coal is 13x10^{-6} g-mole/g-coal, when the coal is soaked for the second time in the toluene aqueous solution, while adsorption of toluene on the coal is 12x10^{-6} g-mole/g-coal for the third time (see Figure 1). Some toluene adsorbed on the coal surface may be not leached out during washing the coal with neat water. These data may suggest that some toluene is adsorbed irreversibly on the coal surface.

Adsorption of toluene on Wyodak coal is 140x10^{-6} g-mole/g-coal in aqueous solution, whereas adsorption of toluene on Pittsburgh seam coal is 23-29x10^{-6} g-mole/g-coal. This data may indicate that Wyodak coal is more reactive to toluene than Pittsburgh coal, and affinity of Wyodak coal for toluene is higher than affinity of Pittsburgh seam coal for toluene.

Experiments for adsorption of isopropanol (IPA) on the untreated Wyodak coal sample were repeated four times to identify

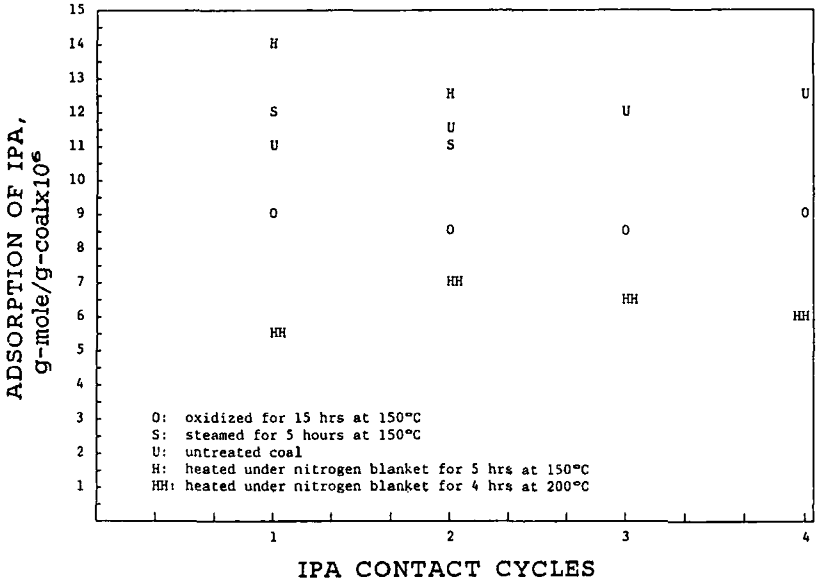

Figure 2. Adsorption of isopropyl alcohol (IPA) on 100-140 mesh Wyodak coal in 0.0399 w % IPA aqueous solution at 32°C.

irreversible adsorption of IPA on Wyodak coal (see Figure 2). Adsorption of IPA on Wyodak coal increases slightly with increased contact cycles. IPA washes out the surface of untreated Wyodak coal, and then more surface accessible to IPA may be available with increased contact cycles. IPA swells untreated Wyodak coal particles, and then adsorption of IPA on Wyodak coal may be increased. This fact may indicate that untreated Wyodak coal is cleaned of surface dirt and swells in the presence of IPA.

Adsorption of IPA on treated Wyodak coals was investigated in the 0.0399 wt % IPA aqueous solution at 32°C to identify effects of treatment on changes in the surface properties of Wyodak coal. Wyodak coal was steamed for 5 hrs at 150°C to eliminate some water-soluble compounds from the coal surface. Wyodak coal was heated under nitrogen blanket for 5 hrs at 150°C. Wyodak coal also was heated under nitrogen blanket for 4 hrs at 208°C. Some Wyodak coal was oxidized for 15 hrs at 150°C.

The treatments of Wyodak coal such as steaming and heating at 150°C do not affect significantly affinities of Wyodak coal for IPA. These observation may suggest that Wyodak coal is quite stable at 150°C. Adsorption of IPA on the Wyodak coal heated at 208°C is lower than the untreated coal as well as the coal heated at 150°C. This observation may indicate that hydrophilic volatile compounds are liberated from the coal surface at 208°C, and affinities of Wyodak coal for IPA are in decrease.

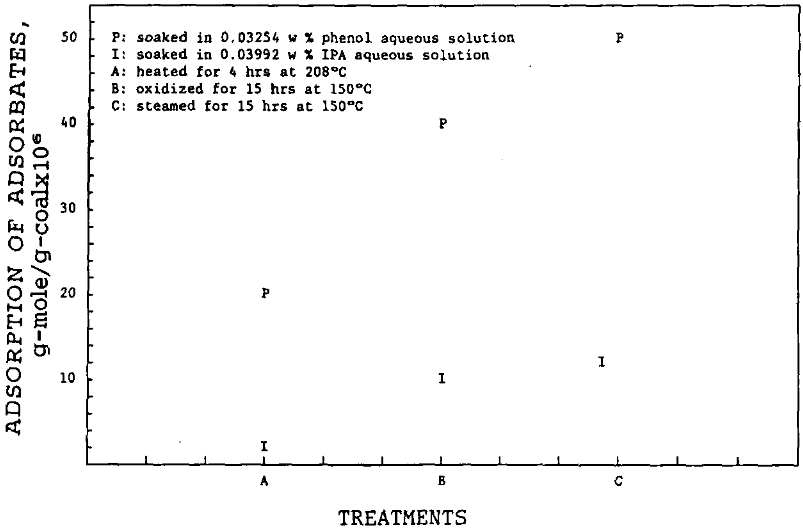

Figure 3. Comparison of adsorption of phenol with adsorption of isopropyl alcohol (IPA) on 100-140 mesh treated Wyodak coal at 32°C.

Adsorption of IPA on the Wyodak coal oxidized at 150°C is lower than adsorption of IPA on the coal heated at 150°C. This fact may suggest that oxidation of the surface of Wyodak coal may result in polymerization of active functional groups on the coal surface and then reduce affinities of Wyodak coal for IPA (10).

Adsorption of phenol on Wyodak coal is higher than adsorption of IPA on Wyodak coal (see Figure 3). Adsorption of phenol on Wyodak coal is more sensitive to the treatment type than adsorption of IPA on Wyodak coal. This fact may reveal that phenol-soluble compounds are subjected more severely to the treatment than IPA-soluble compounds in Wyodak coal, and affinities of Wyodak coal for phenol are higher than affinities of Wyodak coal for IPA. These facts may indicate that phenolic hydroxyl groups are dominant over alcoholic hydroxyl groups on the surface of Wyodak coal.

Pittsburgh coal was heated under nitrogen blanket for 9 hours at 220°C. Pittsburgh coal also was steamed for 9 hours at 220°C. Pittsburgh coal was oxidized for 19 hours at 150°C. Adsorption of phenol on the untreated Pittsburgh coal is lower than adsorption of phenol on the oxidized Pittsburgh coal as well as the steamed Pittsburgh coal (see Figure 4). These data may indicate that the oxidation of Pittsburgh coal at 220°C increases phenolic hydroxyl groups on the coal surface, and steam dissolves some

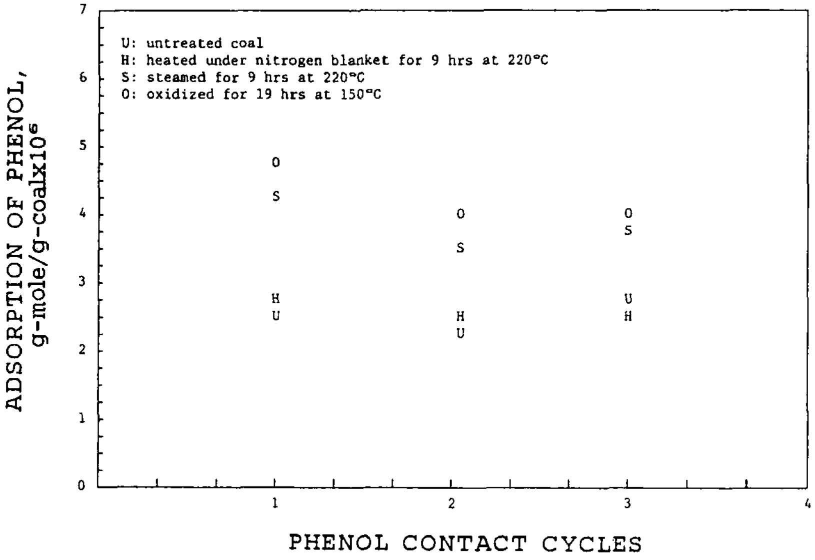

Figure 4. Adsorption of phenol on 100-140 mesh Pittsburgh coal in 0.03254 w % phenol aqueous solution at 32°C.

water-soluble compounds as well as labile compounds on the coal surface so as to increase accessibility of phenol to the coal surface.

Adsorption of phenol on the untreated Pittsburgh coal is almost same as adsorption of phenol on the Pittsburgh coal heated under nitrogen blanket for 9 hours at 220°C. This observation may indicate that heating Pittsburgh coal at 220°C does not change significantly affinity of Pittsburgh coal for phenol.

Adsorption of phenol on Wyodak coal is much higher than adsorption of phenol on Pittsburgh seam coal, as shown in Figures 3 and 4. Effects of the treatments such as oxidizing and steaming on adsorption of phenol on Wyodak coal are more pronounced than that on Pittsburgh coal. These observation may suggest that Wyodak coal has more phenolic hydroxyl groups than Pittsburgh coal, and Pittsburgh coal is stabler than Wyodak coal.

Adsorption of phenol on the oxidized Pittsburgh coal is higher than adsorption of phenol on the steamed Pittsburgh coal (see Figure 4), whereas adsorption of phenol on the oxidized Wyodak coal is lower than adsorption of phenol on the steamed Wyodak coal

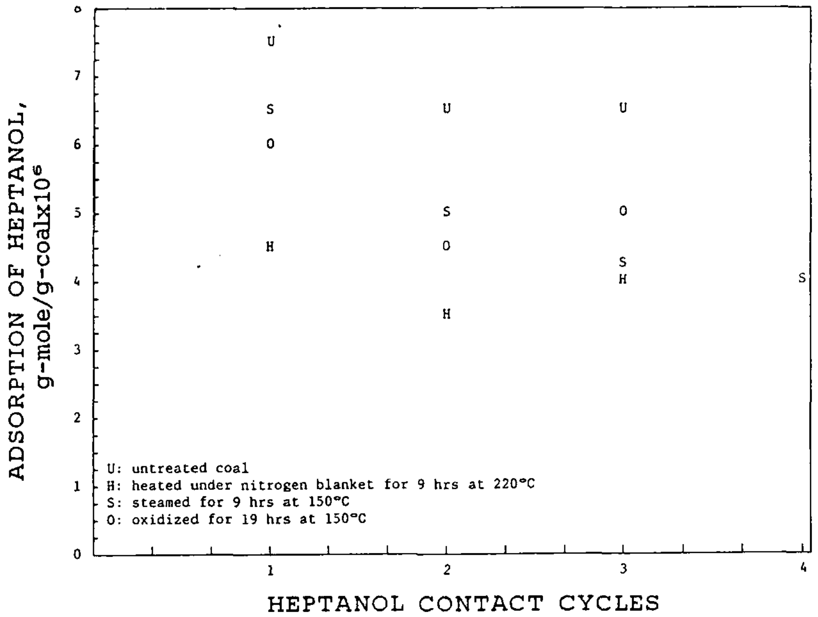

Figure 5. Adsorption of heptanol on 100-140 mesh Pittsburgh coal in 0.03729 w % heptanol aqueous solution at 32°C.

(see Figure 3). These facts may reveal that effects of oxidation on adsorption of phenol on Wyodak coal are less significant than those on Pittsburgh coal, since Wyodak coal contains more oxygen than Pittsburgh coal.

Adsorption of phenol on the Pittsburgh coal heated for 9 hrs at 220°C is slightly higher than adsorption of phenol on the untreated coal. This observation may indicate that some compounds affined to phenol are stable under nitrogen blanket at 220°C.

Pittsburgh coal was steamed, heated and oxidized to identify changes in the surface properties of Pittsburgh coal. Adsorption of heptanol on the untreated Pittsburgh coal is higher than adsorption of heptanol on the treated Pittsburgh coals (see Figure 5). Adsorption of heptanol on the untreated Pittsburgh coal is much higher than the heated Pittsburgh coal. This observation may indicate that some volatile compounds affined to heptanol are detached from the coal surface during heating Pittsburgh coal under nitrogen blanket for 9 hours at 220°C.

Adsorption of heptanol on the oxidized Pittsburgh coal is higher than adsorption of heptanol on the heated Pittsburgh coal. These data may indicate that oxidizing Pittsburgh coal for 19 hours at 150°C increases the surface active sites

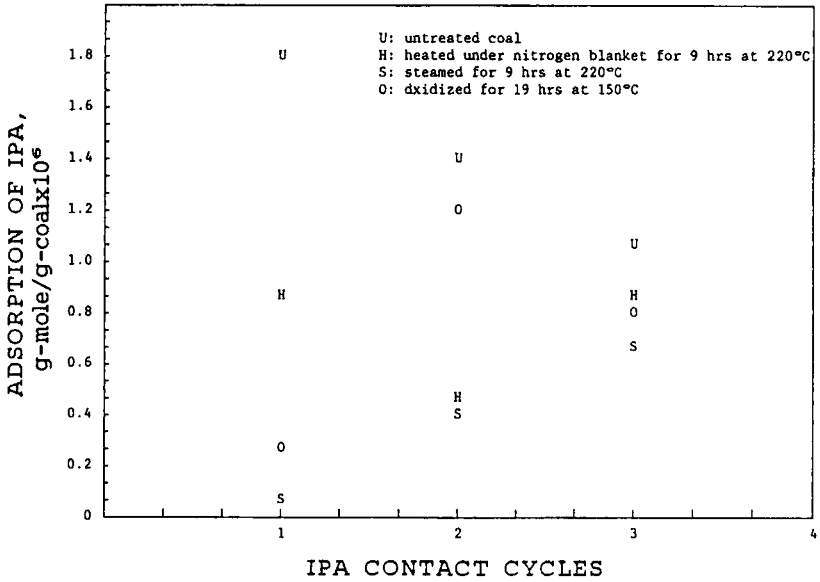

Figure 6. Adsorption of isopropanol on 100-140 mesh Pittsburgh coal in 0.0399 w % IPA aqueous solution at 32°C.

accessible to heptanol. Adsorption of heptanol on the steamed

Pittsburgh coal decreases with increased contact cycles of heptanol. This observation may suggest that adsorption of heptanol on the steamed Pittsburgh coal is irreversible or some compounds are detached from the coal surface along with heptanol during washing the heptanol-adsorbed steamed coal with neat water.

Adsorption of isopropanol on the untreated Pittsburgh coal is higher than adsorption of isopropanol on the treated Pittsburgh coals (see Figure 6). Adsorption of isopropanol on the untreated Pittsburgh coal decreases with increased contact cycles. This observation may suggest that adsorption of IPA on Pittsburgh coal is irreversible or some compounds affined to IPA are extracted from the surface of the untreated Pittsburgh coal during washing the IPA-adsorbed Pittsburgh coal with neat water. Adsorption of isopropanol on the steamed Pittsburgh coal increases with contact cycles of IPA. The steamed Pittsburgh coal may swell in contact with IPA aqueous solution, or the surface area of the steamed Pittsburgh coal increases with increased contact cycles of IPA.

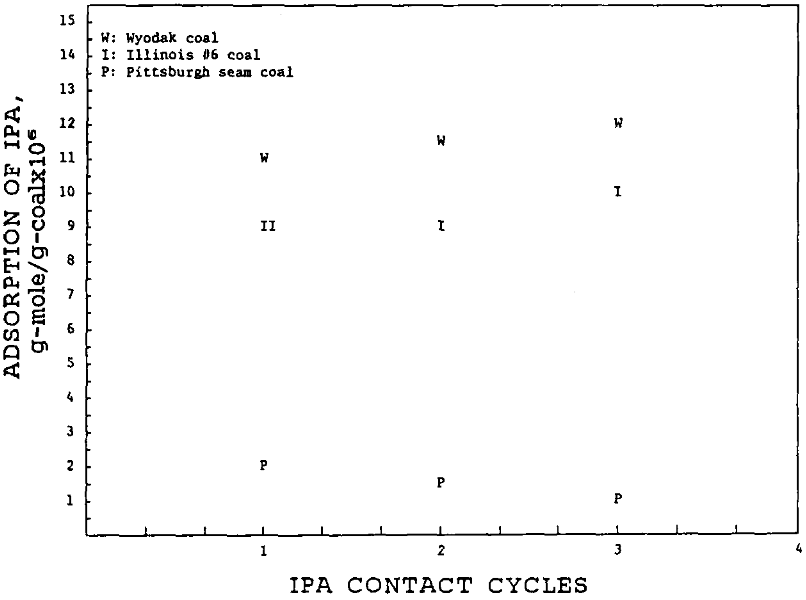

Figure 7. Adsorption of isopropanol (IPA) on 100-140 mesh untreated coals in 0.0399 w % IPA aqueous solution at 32°C.

The plot on adsorption of isopropanol on the oxidized Pittsburgh coal vs. contact cycles of IPA is concave upward as shown in Figure 6. Aqueous isopropanol solution may wash the polymerized surface of the oxidized Pittsburgh coal during the adsorption and washing period, resulting in the increased adsorption of IPA during the first/second contact period. Some IPA is adsorbed irreversibly on the oxidized Pittsburgh coal, resulting in the decreased adsorption of IPA during the second/third contact period.

The plot on adsorption of isopropanol on the heated Pittsburgh coal vs. contact cycles of IPA is concave downward, as shown in Figure 6. Isopropanol may be irreversibly adsorbed on the surface of the heated Pittsburgh coal and be desorbed slowly during the washing period, resulting in the decreased adsorption of IPA on the heated Pittsburgh coal during the first/second contact period and the increased adsorption of IPA on the heated Pittsburgh coal during the second/third contact period.

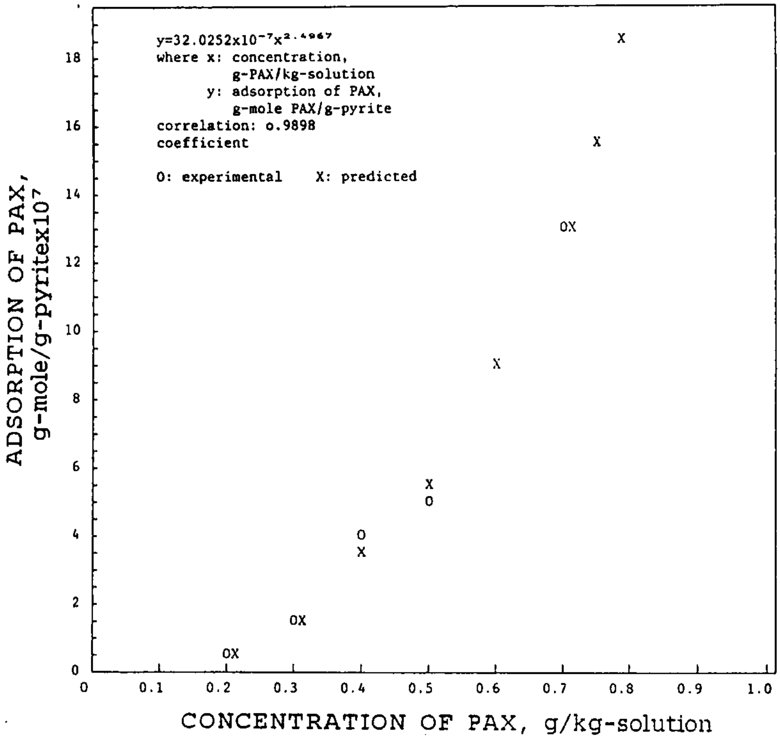

Figure 8. Adsorption of potassium amyl xanthate (PAX) on 117 mesh Rico Colorado pyrite at pH 3.9 and 25°C.

Adsorption of phenol on the treated Pittsburgh coals is higher than adsorption of phenol on the untreated Pittsburgh coal (see figure 4), whereas adsorption of both IPA and heptanol on the treated Pittsburgh coals is lower than adsorption of both IPA and heptanol on the untreated Pittsburgh coals (see Figures 5 and 6). These data may indicate that adsorption sites for phenol increase on treating Pittsburgh coal, whereas adsorption sites for both isopropanol and heptanol decrease on treating Pittsburgh coal.

Adsorption of phenol on Pittsburgh coal increases on treating Pittsburgh coal with steam and air, whereas adsorption of both IPA and n-heptanol on Pittsburgh coal decreases on treating Pittsburgh coal with steam and air. These facts may indicate that both steam and air decrease compounds affined to alcoholic hydroxyl groups and increase compounds affined to phenolic hydroxyl groups on the surface of Pittsburgh coal.

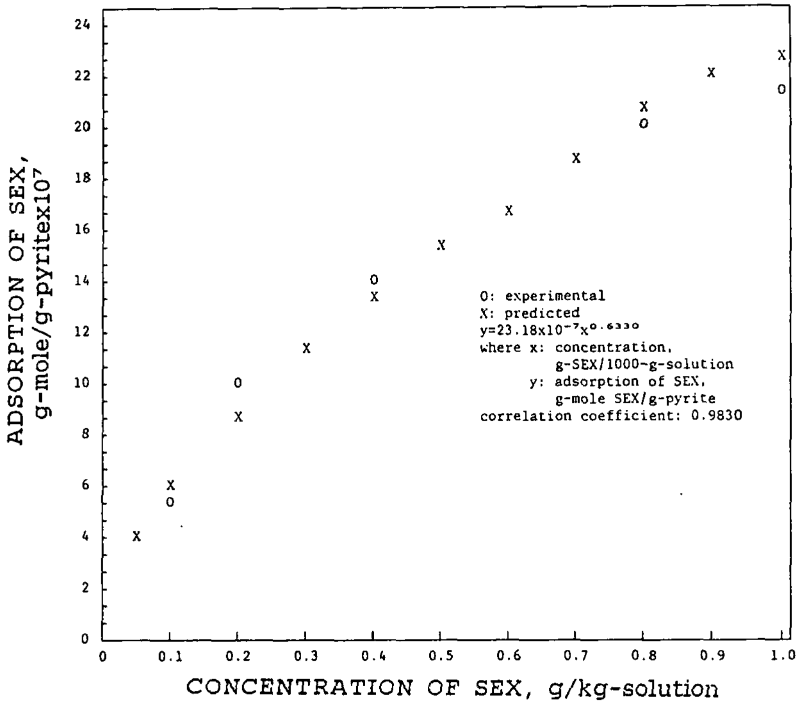

Figure 9. Adsorption of sodium ethyl xanthate (SEX) on 117 mesh Rico Colorado pyrite at pH 3.9 and 25°C.

Adsorption of heptanol on the Pittsburgh coal heated under nitrogen blanket for 9 hrs at 220°C is lowest among the treatments, whereas adsorption of IPA on the Pittsburgh coal steamed for 9 hrs at 220°C is lowest among the treatments. These data may show that heating Pittsburgh coal at 220°C results in removing some compounds affined to higher-aliphatic alcohols from the coal surface and steaming Pittsburgh coal at 220°C results in liberating some compounds affined to alcoholic hydroxyl groups from the coal surface.

Adsorption of IPA on the untreated coals is compared, as shown in Figure 7. Adsorption of IPA on Wyodak coal is higher than adsorption of IPA on Illinois #6 coal, while adsorption of IPA on Pittsburgh coal is much lower than adsorption of IPA on both Wyodak coal and Pittsburgh coal. These facts may indicate that Wyodak coal contains most compounds affined to alcoholic hydroxyl groups among these coals, whereas Pittsburgh coal contains least compounds affined to alcoholic hydroxyl groups among these coals.

Adsorption of heptanol on Pittsburgh coal is much higher than adsorption of IPA on Pittsburgh coal (see Figures 5 and 6). This observation may suggest that compounds affined to higher alcohols are dominaant over compounds affined to alcoholic hydroxyl groups on the surface of Pittsburgh coal.

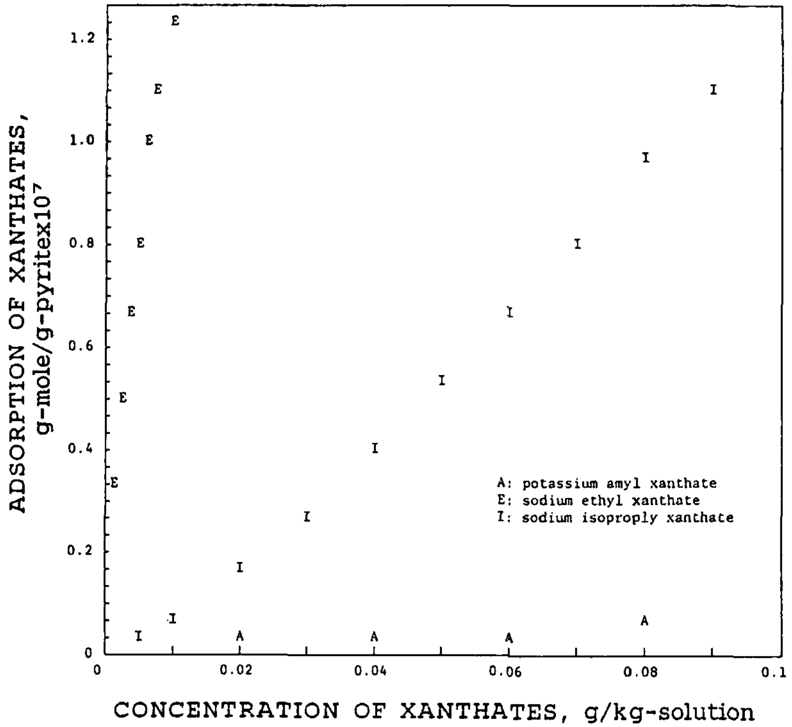

Figure 10. Predicted adsorption of xanthates on 117 mesh Rico Colorado pyrite at various low concentrations, pH 3.9 and 25°C.

Adsorption of xanthates on minus 117 mesh Rico Colorado pyrite was investigated in pH 3.9 aqueous solution at 25°C. Sodium ethyl xanthate, sodium isopropyl xanthate and potassium amyl xanthate supplied by American Cyanamid were used for this study. Experiments for adsorption of xanthates on the pyrite were carried out with the inverse chromatography technique (25).

Equilibrium adsorption of xanthates on the pyrite increases with increased equlibrium concentrations of xanthates (see Figures 8 and 9). Adsorption of the xanthates on the pyrite decreases with increased lengths of the hydrocarbon chains of the xanthates.

Predicted adsorption equations for sodium ethyl xanthate (SEX), sodium isopropyl xanthate (SIX) and potassium amyl xanthate (PAX) are developed by applying the experimental data to the Freundlich isotherm equation through the least squares method, as shown in equations 1 through 3.

$$y=23.18\times10^{-7}x^{0.6330} \qquad (1)$$

where x: concentration of sodium ethyl xanthate, g-SEX/kg-solution.
y: equilibrium adsorption of SEX, g-mole-SEX/g-pyrite.
correlation coefficient: 0.9830

$$y=22.68\times10^{-7}x^{1.2550} \qquad (2)$$

where x: concentration of sodium isopropyl xanthate, g-SIX/kg-solution.
y: equilibrium adsorption of SIX, g-mole-SIX/g-pyrite.
correlation coefficient: 0.9200

$$y=32.03\times10^{-7}x^{2.4967} \qquad (3)$$

where x: concentration of potassium amyl xanthate, g-PAX/kg-solution.
y; equilibrium adsorption of PAX, g-mole-PAX/g-pyrite.
correlation coefficient: 0.9898

Equilibrium adsorption of the xanthates on the pyrite in low-concentration aqueous solution is very difficult to be analyzed with the inverse chromatography technique, because some compounds leach out from the pyrite surface during adsorption process of xanthate on the pyrite and mask actual adsorption of xanthate in the analysis of concentrations of xanthates. Equilibrium adsorption of the xanthates on the pyrite in low-concentration aqueous solution is predicted from the developed equations (see Figure 10).

The complete coverages of the xanthates on the pyrite are determined from chromatographic responses (see equations 4 through 6). Equilibrium adsorption peaks of xanthates on pyrite as a packing material are smaller than eqilibrium adsorption peaks of xanthates on the reference packing material (stainless steel) below an equilibrium concentration for a complete coverage, since some compounds leached out from the coal surface reduce actual peak responses monitored with a refractive index detector. Chromatographic peak height ratios of equilibrium adsorption peaks of xanthates on the pyrite to those on the reference packing become unity, when pyrite is covered completely with xanthate films.

Chromatographic peak height ratios of equilibrium adsorption peaks of xanthates on the pyrite to those on the reference packing are related to equilibrium concentrations of xanthates through the least squares method to predict concentrations of xanthates at a complete coverage of the xanthates on the pyrite (see Figures 11 and 12).

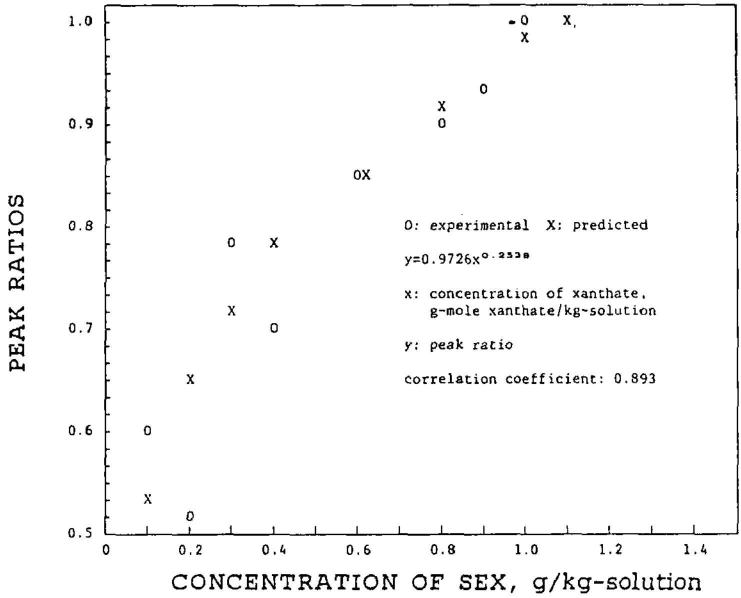

Figure 11. Chromatographic peak height ratios of equilibrium adsorption peaks of sodium ethyl xanthate (SEX) on the pyrite to those on the reference packing material at various concentrations of SEX, 23-25°C and pH 3.9.

$$y=0.9726x^{0.2538} \qquad (4)$$

where x: concentrations of SEX, g-mole-SEX/kg-solution
y: peak ratios
correlation coefficient: 0.893

$$y=0.9241x^{0.2081} \qquad (5)$$

where x: concentrations of SIX, g-mole-SIX/kg-solution
y: peak ratios
correlation coefficient: 0.9710

$$y=0.8424x^{0.2410} \qquad (6)$$

where x: concentrations of PAX, g-mole-PAX/kg-solution
y: peak ratios
correlation coefficient: 0.9743

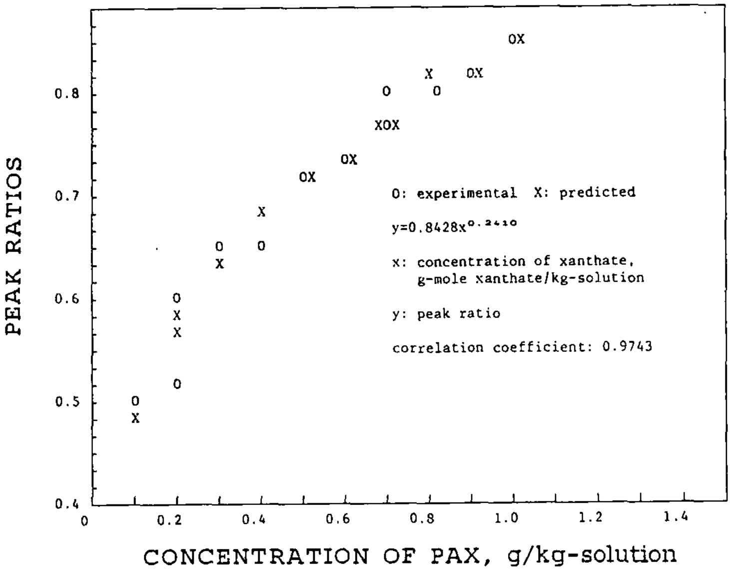

Figure 12. Chromatographic peak height ratios of equilibrium adsorption peaks of potassium amyl xanthate (PAX) on the pyrite to those on the reference packing material at various concentrations of PAX, 23-25°C and pH 3.9.

CONCLUSIONS

The following conclusions are drawn from our experimental data, which were obtained from the inverse chromatography technique, using various probe compounds as adsorbates and various coals as adsorbents.

1. Toluene is adsorbed irreversibly on Pittsburgh coal. Heating Pittsburgh coal at 220°C does not change significantly affinity of Pittsburgh coal for phenol. Adsorption sites for phenol increase on treating Pittsburgh coal, whereas adsorption sites for both isopropanol and heptanol decrease on treating Pittsburgh coal.

2. Wyodak coal is quite stable at 150°C. Hydrophilic volatile compounds appear to be liberated from Wyodak coal at 208°C. Phenol-soluble compounds are subjected more severely to the coal treatements that IPA-soluble compounds in Wyodak coal.

Phenolic hydroxyl groups are dominant over alcoholic hydroxyl groups on the surface of Wyodak coal.

3. Affinity of Wyodak coal for toluene is higher than affinity of Pittsburgh coal for toluene. Wyodak coal has more phenolic hydroxyl groups than Pittsburgh coal.

4. Concentrations of xanthates for a complete coverage of a xanthate on a pyrite can be determined with the inverse chromatography technique.

ACKNOWLEDGEMENTS

This research work was supported by the U. S. Department of Energy and the Oak Ridge Associated Universities. The authors wish to acknowlege Mr. Robert H. Lowman for his assistance in this research work at the Pittsburgh Energy Technology Center.

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