The Effect of Particle Size on Heat of Immersion of Bituminous High Volatile Pittsburgh Seam Coal

A thesis submitted in partial fulfillment of the requirement for the degree of Master of Science in Metallurgical Engineering

by

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I would also like to thank to Prof. R. Bradt and Prof. J. Hendrix for their participation in guiding me towards the completion of this research work. Finally, I would like to thank Dr. T. G. Melkus for initiating the project and her valuable help.
A Setaram C-80 heat flux calorimeter was used to measure the heat of immersion of Pittsburgh seam coal. The investigation was focussed to determine the effect of the coal particle size on the heat of immersion in water, 20% methanol-water, and an immulsion of flotation agents. Flotation experiments were also performed on all particle sizes to correlate the flotation response with the heat of immersion study.

It is determined that the heat of immersion increases exponentially with decreasing particle size in all immersional liquids. The increase is also seen in the flotation recovery with flotation mixture as immersional liquid. The heat of immersion values are the lowest when flotation agent mixture is used and highest in 20% methanol-water. The high values of \( \Delta H_{imm} \) in 20% methanol-water is due to the more polarity of the mixture which results in a higher capability in complete wetting the coal surface and the ease of penetration by the mixture to the pore structure of coal than other immersional liquids. The decrease in flotation recovery is caused by the decrease in the hydrophobicity of coal as the particle size decrease, which is correlated with the heat of immersion. The low heat of immersion values using the flotation agents mixture are thought to be caused by the difficulty of the immersional liquid to penetrate the pore structure of coal due to the hydrophobic interaction of flotation agent with coal surface.
In all immersional liquids, the slow increase in the heat of immersion is observed at low surface area indicating the initial incomplete wetting of the coal surface.
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1.0 INTRODUCTION

Coal has become an increasingly important resource for energy and chemical feedstock. The conventional coal cleaning process uses gravity method to handle coal of 28 mesh or coarser. Much of finer coal is lost or intentionally discarded in many coal industries throughout the country. Several processes are known to offer in the recovery of fine coal such as selective coalescence and froth flotation. The recovery processes are of considerable importance from the environmental and economic standpoints.

Coal exhibits natural floatability and its response to flotation varies with carbon content as well as ash content. With regard to ash content, Gaudin observed that the greater the ash content of coal, the less hydrophobic is the coal. Although coal possesses natural hydrophobicity, its surface exhibits hydrophilic sites and its flotability varies considerably with the rank and its origin. The use of chemical additives in coal flotation is mandatory in order to achieve the optimum recovery. These additives can alter the state of coal surface properties by means of chemical and/or electrostatic interactions.

Heat of immersion measurements can be used to characterize a solid in terms of hydrophobicity or hydrophilicity and its values are important in investigating the surface properties of solid. The main purpose of this research work is to seek a better understanding of correlation between the heat of immersion of coal and particle size. The study of coal surface properties is crucial
in the development of most effective coal cleaning techniques to yield the cleanest possible coal. The heat of immersion measurements are conducted using a Setaram C-80 Heat Flux microcalorimeter, while the surface area determinations are performed at Pittsburgh Energy Technology Center (PETC). The heat of immersion study can be used to characterize a solid in terms of hydrophobicity or hydrophilicity and its values are important in investigating the surface properties of solid.
2.0 LITERATURE REVIEW

A detailed description of microcalorimetry, thermodynamics of wetting and adsorption, and also site energy distribution were fully presented by Boyd and Harkins\(^\text{a}\) as well as Chessick and Zettlemoyer\(^\text{b}\). A number of heat of immersion experiments were conducted on hydrophobic and hydrophilic solids, such as rutile, clay, graphon, calcium, fluoride, teflon, etc. using different kinds of liquids (i.e., organics, surfactants, water, etc.) for the purpose of evaluating the solid surface properties of wettability, surface polarity and site energy distribution\(^{4,5,6,7}\).

There are numerous methods to determine the heat of immersion and were carried out by various researchers over the years. The results of such variety of techniques were neatly compiled and compared by Eatough and Hansen\(^\text{b}\).

2.1 Heat of Immersion of Coal.

The most recent and best described work on the heat of immersion of coal was conducted by Melkus et al.\(^\text{a}\). The work involved the measurements of heat of immersion of six different kinds of coal and determined the differences in surface properties owing to coal rank, surface oxidation state, moisture content, and petrographic constituent content. In addition the characterization of six coals and other solids (i.e., pyrite, kaolin, slate and graphite) was performed in terms of relative hydrophobicity or
hydrophilicity by means of comparison of the data on heat of immersion in methanol and water.

The presence of water in moist coal remains a mystery and is not well understood at the moment. This moisture occurs in a wide variety of both physically and chemically bonded forms, and its existence influences various coal properties. The most direct method for assessing the thermodynamics of the interaction of water with coal is to measure the heat of immersion (frequently referred to as heat of wetting).

Glanville et al.\(^4\) has shown the relationship of moisture content with the heat of immersion of a subbituminous coal, Wyodak No. 3 in water. They concluded that the heat of immersion decreased smoothly with increasing moisture content over the range from 1% to 15% moisture and found that about 4% residual moisture was still left on the coal when exposing to a vacuum at room temperature. The residual moisture represented a surface coverage of about 2.5 monolayers based on the BET water surface area. It was further established that the first two or three monolayers of adsorbed water were more strongly bonded to the substrate than subsequent layers. The calculated BET water surface area was found to be \(350 \text{ m}^2 \text{ g}^{-1}\), compared with \(7.5 \text{ m}^2 \text{ g}^{-1}\) based on krypton adsorption.

The heat of immersion of coal is considered to be valuable tool in probing the structure and chemistry of coal. Fuller\(^{10}\) reviewed in great detail the studies of heat of immersion with variation of coal rank, particle size, and mineral content. The
lower ranked coals, having a more loosely bound structure and a much higher oxygen and nitrogen content, were noted to have a tenfold increase in the immersional heat value. A trend of increasing heats of immersion of Illinois No.6 and Wyodak coal samples was observed with the decreasing particle size. This was an indication of the dependency of rate of heat evolution on the size of the coals. The heat of immersion was also shown to be greater for the mineral-rich fractions due to the greater polarity of the minerals (SiO₂, Al₂O₃, CaCO₃, etc.) and/or the more open structure due to the mineral-organic interface.

In the search for better understanding of micropore filling phenomenon, Zettlemoyer et al.⁹ conducted the heat of immersion of carbosieve-s, a thermally prepared polymer-based carbon in water, methanol and 2-propanol. The decrease in the heat of immersion was noted until a plateau was reached after approximately 25% of the micropore volume filled. The heat decreased again after 80% of the micropore volume was filled. For the methanol pre-coverage a plateau of heat of immersion was observed at a pre-coverage equivalent to 20% of the micropore volume filled. The decrease was continued at 70% and 93% volume filled. The gradual decrease in the heat was seen up to 34% volume filling for the case of 2-propanol pre-coverage. At approximately 90% micropore filling, the heat of immersion decreased once again.
2.2 The Heat of Immersion on Surface Oxidized Coal

The state of oxidation of coal affects a number of processes such as liquefaction\(^{(11)}\), coking\(^{(12,13)}\) and flotation\(^{(14)}\). These processes are very much dependent on the coal surface as well as the interaction of a liquid with the surface. The factors that were responsible for surface oxidation of coal were due to storage temperature\(^{(15)}\) and exposure to ultraviolet light\(^{(13)}\). Perry and Grint\(^{(16)}\) further concluded that surface oxygen content varied with the coal rank, decreasing from anthracite to lignite.

The effects of coal oxidation on the heat of immersion were fully investigated by Wightman et al.\(^{(6)}\) using Virginia - C coal. The coal was preheated in air for 24 hours between 125 and 320\(^{0}\) C, and found that there was nearly fifty-fold larger heat of immersion for coal heated at 320\(^{0}\) C than for the unheated coal. The small increase was observed up to about 150\(^{0}\) C. The sudden change in heat of immersion of coal at several elevated temperatures was analyzed by the use of ESCA (Electron Spectroscopy for Chemical Analysis) which determined the surface oxygen content of the thermally treated coals. The study lead to the conclusion that the heating up of the coal up to 320\(^{0}\) C increased the heat of immersion which was due to the increasing number of surface \(\text{C} - \text{O}\) groups on the surface.

The effects of oxidized coal in water on the heat of immersion were determined by Hollenhead et al.\(^{(17)}\) on Pocahontas No. 3 coal. The pretreatment of the coal was carried out by means of
solvent extraction utilizing methanol and pyridine. They observed that there was no difference in the heat values in water for methanol-extracted, pyridine-extracted and unextracted coal as a function of oxidation time at 320°C. The results indicated that prior extraction with methanol or pyridine had no effect on the heat of immersion of either unoxidized or oxidized coal in water. The immersion times of the unextracted and extracted coals versus oxidation time were also investigated. The immersion times for the unextracted coal were found to be longer than those of the extracted ones. This suggested that the shorter immersion times for the extracted coal did create an increase in the water accessibility to the pore structure of coal and produced no new surface area which would otherwise result in the higher heat of immersion. The extraction with pyridine on coal which lead to the shortening of immersion times indicated that the solvent did not only swell the coal, but also extracted the material from it\(^{(18)}\) thus creating a better access for water to the surface. This phenomenon of swelling was attributed to the formation of hydrogen bonding to the macromolecular network of the coal. Larsen et al.\(^{(19)}\) observed similar swelling of bituminous coal using various solvents, including pyridine, and demonstrated that the degree of swelling by one solvent was significantly different from the others.
2.3 The Heat of Immersion by Organic Solvents

Widyani and Wightman\textsuperscript{(20)} used a homologous of n-alcohols as immersion liquids in the heat of immersion studies in an attempt to understand the thermodynamics and kinetics of immersion of Pocahontas No. 3 coal at 36° C. The measurements were done by utilizing a Calvet MS 70 microcalorimeter and the C\textsubscript{1} to C\textsubscript{12} n-alcohol were used as the solvents. A trend of decreasing values of heat was noted as the n-alcohol chain length increased. This is a direct contrast to the observation made by Clint et al.\textsuperscript{(21)} who performed the heat of immersion of Graphon indicating that the increase was non-linear to the increase in the n-alcohol chain length. The kinetics of immersion in methanol was found to be the fastest while for the case of n-butanol it was the slowest. The interpretation of such behavior in the kinetic of immersion or the time required to return to steady state, can be provided in terms of the degree of penetration of the solvents into the pore structure and methanol seemed to be able to do so with ease. This would consequently result in the higher heat of immersion. The puzzling trend of increasing immersion times up to n-butanol and decreasing steadily for n-pentanol and higher chain length were observed. The n-alcohols of ethanol, n-propanol and n-butanol were able to penetrate the smallest micropores with more difficulty which resulted in the increase in the kinetics of immersion. As carbon chain length continued to increase, the accessibility of smallest pores became minimal which in turn lowered the heat of
immersion and speeded up the immersion kinetics.

Glanville and Wightman(22) investigated the wetting of powdered coals by alkanol-water solutions and other liquids. The Pocahontas No. 3 coal was used and its critical surface tension of 0.033 J m$^{-2}$ was estimated from the measured wetting concentrations. By varying the concentration of alkanols on both Pocahontas No. 3 and NBS - SRM 1632a coal dust, they discovered that the wetting of coal was possible at reasonable concentrations of 30 mole % methanol and above in the methanol-water mixtures. The findings suggested that there was a critical concentration necessary to wet the coal for each alkanol. The other observations made during the experiments were that the critical wetting concentration shifted progressively to lower values as the carbon chain length of the alkanols increased, which was attributed to the increase surface activity of alkanols(23). The heat of immersion in methanol-water mixtures was carried out with the aid of a Calvet MS 70 microcalorimeter and the results of measurements indicated the variation with the mixture concentration. A maximum heat of immersion of about 16 J g$^{-1}$ was obtained with methanol concentrations above 30 mole% which lead to the conclusion that methanol was the principal adsorbate in these solutions. A concentration of methanol of 20 mole% or less was found to be incapable of wetting the coal dust. The immersional heats for Pocahontas No. 3 coal were observed to vary when using various organic solvents. Methylene chloride solvent showed the greatest value and hexane the least, while alkanols yielded intermediate
values. The authors indicated that for all organic solvents, the release of the heat of immersion could take place over a long period of time of up to nine hours.

The thermodynamics of acid-base interactions of three coal samples of different ranks at elevated temperatures was studied in detail by Chawla and Arnett(24). The type of coals used were Wyoming Rawhide subbituminous, Texas Big-Brown lignite, and Illinois No.6 bituminous. The heat of reaction ($\Delta H_{rxn}$) for these coals were measured in aqueous tetrabutylammonium hydroxide (TBAH) at $80^\circ C$ temperature using a Setaram C-80 calorimeter. According to $\Delta H_{rxn}$ values, the acidity of the coals is ranked in the following decreasing order of exothermicity: Wyoming Rawhide > Texas Big-Brown > Illinois No.6. The effect of particle size of Rawhide coal was also investigated and it was found that $\Delta H_{rxn}$ values were independent of various sizes of coal. There were 31 basic liquids used in the heat of immersion studies on Rawhide coal at $80^\circ C$ and $120^\circ C$. It was determined that the straight-chain aliphatic compounds have higher heat of immersion than the rest of the organic liquids. No significant correlation between the heat of immersion and the heat of protonation of the basic solvents by the superacid HSO$_3$F was observed. The overall behavior is indicative of combination of processes of proton transfer and hydrogen bonding with a strong influence from steric interactions. Using only 12 basic liquids selected from a list of 31 liquids, thermochemical comparisons of three coal samples were conducted. A good linear correlation was found to exist between the heat of immersion values
of Rawhide subbituminous and Texas Big-Brown for eight liquids. It is interesting to note that although these two coals possess similarity in their mineral compositions and acid-base behavior, the interactions of Rawhide coal are slightly more exothermic than Texas Big-Brown. The Illinois No. 6, on the other hand, showed completely different behavior in the interaction of bases with acidic sites compared to the other two type of coals. The apparent reason for such deviation in behavior of Illinois No. 6 could be attributed to the dissimilarity in mineral content as well as the less accessibility to its acidic structural unit.

2.4 Studies of Surface Area Determination of Coal

Many studies of the fine structure of coal by adsorption methods have been reported. A good number of years have been spent in the selection of suitable adsorbates and temperatures for experimental theories for interpretation of the isotherms, because the structure of coal is complex from both chemical and physical viewpoints.

The determination of surface area does not only offer the advantage of understanding of the coking process and the production of active carbons, but its values are invaluable in the mining of coal where sorbed methane is encountered. The early method for the determination of surface area was by utilization of low angle scattering of x-rays\(^\text{(23)}\). The most recent ones are essentially all methods of adsorption. A number of years were spent by Brunauer,
Emmett and Teller\textsuperscript{(25)} to come up with the adsorption equation, which later known as BET equation, to be applied and correctly interpreted to coals and cokes. The total internal area can be determined by the heat of wetting (HOW) technique which utilizes the calorimeter for measurement. The heat evolved is considered to be the heat of adsorption when a carbonaceous sample is immersed in a liquid, usually methanol. The heat value is in fact a function of the area, per gram of the sample. There had been a strong controversy over the versatility and basic concepts of the HOW method. The lack of agreement on the method was centered on whether or not the lower surface area (1 to 5 m\textsuperscript{2} g\textsuperscript{-1}) obtained from nitrogen isotherms were correct (HOW gave areas of up to 200 m\textsuperscript{2} g\textsuperscript{-1}). The high value of surface area by HOW method was explained by Malherbe\textsuperscript{(27)} who postulated that imbibition of methanol by the coal substance was a cause of the enhanced take-up of methanol and hence high HOW value. The divergence of the results by several authors were proven to be valid with the much wider understanding of the adsorption processes in micropore systems.

Walker and Patel\textsuperscript{(28)} had measured the surface area of several type of coals calculated from carbon dioxide adsorption isotherms at 298 K using the BET equation. The results of the measurement were compared to those of Dubinin-Polanyi (DP) equation for calculating the surface area of coals. In all cases, it was noted that the calculated areas from the BET and DP equations agreed very closely with one another. This suggested that the measurement was possible for adsorption of carbon dioxide in a conventional vacuum
apparatus and area calculated using the DP equation.

The measurement of the surface areas of six coals (200 x 325 mesh) was conducted by Walker and Kini\(^{(29)}\). The surface area was estimated from the sorption of nitrogen at 77 K, krypton at 195 K, carbon dioxide at 195 K, xenon at 273 K, and carbon dioxide at 298 K. The six coals under investigation were Anthracite No.1, Bituminous coal No. 912, 956, 888, 885 and 6 respectively. There are two major problems that need to be addressed in the measurement of surface area by gas adsorption. The first involves the possibility of activated diffusion which will result in the diminishing surface area available to the sorbate. The other problem is to determine the fraction of area to be occupied by the sorbate molecule. The surface area from nitrogen adsorption at 77 K appeared to be low by about an order of magnitude which lead to the belief that activated diffusion was taking place in the small coal particles. The activated diffusion limitations due to temperature for carbon dioxide adsorption at 195 K and 298 K were at a minimum. The finding was based on the fact that carbon dioxide having a small dimension (5.8 A in length and 3.7 A in width)\(^{(29)}\) has a relatively high critical temperature, 304 K. The higher surface area reported on coal No. 6, as measured by carbon dioxide sorption at 195 K than at 298 K was explained in terms of the differences in the packing density of sorbed carbon dioxide rather than on the basis of activated diffusion theory. The overall conclusion was drawn to the fact that the carbon dioxide sorption system seemed to offer the most promising results in the
measurement of more complete surface areas using the BET equation on the microfine structure of coal.
3.0 CALORIMETRY

3.1 Technical Background

The standard free energy of adsorption of one component from a dilute solution may be estimated from the adsorption data by application of the Langmuir equation and from measurements of adsorption at different temperatures\(^{'31,32}\). However, this procedure can give misleading results. Direct calorimetry is the only method to obtain reliable enthalpy data. Perhaps the earliest use of calorimetric measurements was back in 1904 by Dewar\(^{33}\) and the frequent application of the instrument was very limited due to the numerous technical difficulties and uncertainty in the interpretation of the results. The advancement and development of new electronic technologies have made it possible to overcome many of previously encountered difficulties and has created more reliable instruments.

Generally, there are two types of calorimeters commonly used to study the adsorption process. The first involves the measurement of the heat evolved when the evacuated solid adsorbent is brought into contact with the solution in the calorimeter. The solid is contained in a bulb which is broken beneath the surface of the solution. Since the composition of the adsorbed layer is different from that of the bulk liquid, it is normally necessary to measure the heat change associated with this dilution, and this may be achieved by breaking an evacuated bulb containing the solute
into the solvent, corrections being made for the heat of the bulb breaking and the evaporation of the solvent into the empty space in the bulb. The variation in the heat of immersion of the solid in the solution is determined at constant temperature, and is compared with the adsorption isotherm to give the differential enthalpy of adsorption.

The second type of calorimetric technique involves a flow system. A known quantity of solution is injected into a stream of solvent flowing through a column of adsorbent contained in the calorimetric cell. The heat change recorded by this procedure is essentially an enthalpy of displacement and may be related to an adsorption isotherm to yield enthalpies of adsorption. This type of flow microcalorimeter is available commercially and has been used extensively by a number of research workers.

3.2 Solution Delivery Techniques

Izatt et al.\(^{(4)}\) discussed in considerable detail the methods of introduction of solution into the calorimeter. There are basically four methods considered here and they are: 1) titration, 2) direct injection, 3) flow, and 4) batch. In the titration type of delivery, a continuous amount of titrant is introduced into a reaction vessel with the aid of either a motorized syringe-type buret or gravity-flow thermostated buret. The heat generated in the vessel is a function of volume of titrant or time. The excess titrant is delivered very quickly into the reaction vessel for the
injection method. The measurement of temperature change is then conducted. Unlike the above two techniques, the flow type calorimeter utilizes two or more streams of reactants into the mixing vessel whereby the heat produced is monitored as a function of temperature change. The batch calorimeter, on the other hand, is characterized by the confinement of one reactant and another in the glass ampoule.

3.3 Types of Calorimeters

By calorimetric measurement, the heat of adsorption, the heat of desorption and the heat capacity of the adsorbed phase or the heat of immersion can be determined. The various instruments may be classified, for example, according to 1) the nature of the adsorbent (powder, film, filament, ribbon), 2) the temperature regime of the calorimeter (isothermal, adiabatic and diathermic calorimeters), 3) the temperature of the measurement, 4) the sensitivity and precision of the measurement, 5) the sensor used to indicate the thermal processes in the calorimeter, and 6) the type of apparatus (the single calorimeter or the twin calorimeter). Several of the most common calorimeters will be discussed in the following sections.

3.3.1 Specially Designed Calorimeter for Powdered Adsorbents.

Most of the applications of calorimeters are for the measurements of the heat of adsorption or desorption on powder.
They essentially consist of a calorimetric vessel containing the adsorbent, surrounded by protective jacket or shield and external thermostat. It is possible to divide the calorimeters into three groups. In isothermal calorimeters, the temperature of the vessel is permanently constant. In adiabatic calorimeters, all of the heat liberated remains in the vessel, thus raising its temperature. Diathermic calorimeters, often called isoperibol or constant-temperature-environment calorimeters, operate on the basis of a finite and defined rate of dissipation of the heat evolved in the vessel to the thermostat; the vessel temperature rises at first, returning to its initial value after the completion of the heat-liberating process.

3.3.1.1 Diathermic Calorimeters. This type of calorimeter consists of a thin-walled cylindrical platinum vessel, located in a glass jacket which can be evacuated. A perforated platinum tube passes through the center of the platinum vessel. The temperature measuring junction of a copper-constantan thermocouple is soldered onto the outside of the platinum vessel, the reference junction being attached to the jacket. The jacket is immersed in a thermostatically controlled bath. The output voltage of the thermocouple can be fed to a sensitive galvanometer or, better, it can be amplified and coupled to a chart recorder. The heats of adsorption measured by this type of calorimeter produce the results with overall accuracy of from ± 2.5 to ± 5 %. The amount of heat liberated in one adsorbate dose is usually of the order $10^4$ cal.
The calorimeter has been widely used for measurements from 77 K to room temperature. Garden et al. perfected the calorimeter in order to measure heats of adsorption at 90 K with an absolute precision of ± 25 cal/mole even with this low rate of heat evolution, when the measurement extended over several hours.

3.3.1.2 Adiabatic Calorimeters. The basic idea of adiabatic calorimeters is to keep all of the heat evolved in the adsorption process inside of the calorimetric vessel by preventing any heat losses to the environment. This is accomplished by controlling the temperature of the environment such that it is always at the temperature of the vessel. The required amount of heat liberated in the vessel is then obtained by multiplying the measured temperature rise of the vessel by its experimentally determined heat capacity. The improved version of adiabatic calorimeter is that designed by Kiselev and co-workers which comprises a copper envelope, into which a glass vessel containing the adsorbent fits very closely. The calorimeter is equipped with a constant heat exchange device that eliminates the problem of temperature elevation produced by resistance thermometers. The temperature sensitivity of the calorimeter is 3 x 10^5 degrees, and its heat capacity is 60 cal/deg, so that the thermal sensitivity of the instrument equals to approximately 2 x 10^3 cal. The calorimeter is suitable for measurements at room temperature of adsorption processes in which the heat is liberated for several tens of minutes. It can be easily modified to measure heats of adsorption
under isothermal conditions. The calibration of the calorimeter heat capacity is accurate to between 0.04 and 0.01 per cent. The low-temperature adiabatic calorimeters of similar design and comparable precision (between 0.1 and 1%) and sensitivity have been constructed and widely utilized. The device is typically designed for use in the 10 to 150 K range; calibration of the heat capacity of the empty calorimeter yields results of precision better than 0.03% above 50 K, and better than 0.1% at 30 K. Below 30 K, the decreasing sensitivity of the platinum thermometer is largely responsible for a decrease in the accuracy to 1%.

3.3.1.3 Isothermal Calorimeters. The original concept of an isothermal calorimeter was to measure the amount of ice melted due to heat liberated by the process being studied. The calorimeter is formed by a glass vessel sealed into a jacket fitted with a graduated capillary. The adsorbent is placed in the vessel and a layer of ice is allowed to freeze homogeneously onto the external wall of the vessel before the experiment. The volume decrease resulting from the melting of a part of ice due to the liberation of heat in the vessel, is indicated by a shift of the mercury level in the capillary. The reported sensitivity of the calorimetric measurement was $2 \times 10^{-2}$ cal and the total error in the determined heat of adsorption was less than 1%. The volume changes resulting from the melting of substances other than ice may be used for calorimetric measurement provided that their latent heat of fusion is small (i.e., tens of cal/g), their volume change on melting is
large (at least $10^3$-$10^4$ m/kg), they have a sharp phase transition, can be prepared in a pure state and are sufficiently stable. The modification of isothermal calorimeter was developed to measure the heat of adsorption using a completely different procedure and with constant heat exchange. The temperature of the calorimetric vessel with constant heat exchange to the surrounding shield is maintained constant and slightly higher than that of the shield by a constant power heater. When an exothermic adsorption process starts in the vessel, the heater is intermittently switched off to maintain the temperature of the vessel constant with only very small oscillations. The required heat of adsorption is given directly by the product of the heater power and the sum of time intervals during which it was switched off from the beginning of up to the completion of the adsorption process. As long as there is a good thermal contact between the heater and the vessel, the error does not usually exceed 0.001-0.02 % of the measured value for a total of 50-200 switching operations. Further improvement of the calorimeter was made which extended the use of the instrument to temperatures up to 670 K. The temperature sensitivity of such a device is $1.5 \times 10^3$ degrees, the thermal sensitivity $3 \times 10^4$ cal and the drift of the zero line in the temperature mentioned is of $3 \times 10^5$ deg/h, which corresponds to the absolute error in the measurement of $6 \times 10^3$ cal/h.

Partyka et al.\cite{36} modified the isothermal microcalorimeter basing on the principles of the Microsical flow microcalorimeter\cite{37} for the purpose of measuring the enthalpies of mixing and
adsorption onto finely divided solids suspended in liquids. The device utilized the mechanism of agitation within the calorimetric vessel and two thermistors that served to detect the temperature changes due to chemical and physical effects in the cell study or to the electrical calibration. The main contribution to this development lies in the design of the calorimetric cell, and in the controlled introduction of reagents into the cell. The homogeneity of the solution or suspension is insured by horizontal agitation with a variable speed of rotation to suit the nature of the liquid/solid system investigated. The thermistors, calibration coil and the injection part are immersed in the solution or suspension. A precision syringe pump injects a reagent continuously or discontinuously so that integral or differential molar reaction enthalpies can be measured. The rate of injection can be varied between 0.01 and 0.20 g min\(^{-1}\) without introducing any significant thermal perturbation. The microcalorimeter was tested extensively with satisfactory results at temperatures ranging from 20 to 50° C.

3.3.1.4 Twin Calorimeters. All of the diathermic calorimeters have the characteristics of instruments with only a single calorimetric vessel. The use of two calorimetric vessels, on the other hand, has received tremendous attention by many scientists. They are commonly known as the differential or twin calorimeters. A well-known calorimeter of such a type is the Tian-Calvet calorimeter. The modern version of this instrument has become by
far the most important of the commercially available calorimeters applicable to measurements of heats of adsorption. The characteristics and its technical background will be discussed in the following sections.

3.4 The Setaram C-80 Heat Flow Calorimeter

The type of calorimeter that will be utilized in this research work is that of C-80 Heat Flow calorimeter (Figure 1) which is a heat flux calorimeter based on the Tian-Calvet principle.

3.4.1 Instrument Background

The C-80 calorimeter unit consists primarily of two identical and independent heat flow detectors that are confined in a heat conductive block. The monitoring of temperature change is carried out with the use of a temperature programmer/controller. The high thermal conductivity construction of heat flow detectors are such that the temperature of the block and vessels are identical. Any sudden thermal pertubations to the block are easily eliminated since the detector connection is done differentially, so that the signal generated only by heat exchange with sample is liberated.

3.4.2 Mode of Operation

The principle of operation of C-80 heat flow calorimeter is based on an imposed temperature. There exists a heat transfer measurement between the system under study and the calorimeter
Figure 1. Calorimeter's Internal View
block. The temperature which can be fixed or varied is an experimental parameter and not a calorimetric measurement. This temperature is generated by the thermostated calorimetric block which surrounds the detector and vessels. The calorimetric block constitutes the heat source, or the heat sink, with which the experimental system can indefinitely exchange heat. The fluxmeters which are located between the system and the heat block, are used for the calorimetric measurement. They measure the continuous thermal exchange. The external temperature perturbations in the calorimetric block are eliminated by having two fluxmeters connected differentially so as to cancel any signal other than that due to the system under study.

3.4.2.1 The Continuous Fluxmetric Measurement at Constant Temperature. If one vessel is the source of a continuous and constant power $W$, this power will flow through the thermocouples into the calorimetric block (Figure 2). The various temperatures will be constant as long as the power $W$, is constant. One of the thermocouples $i$, transfers an elementary power $W_i$: there is a very small difference in temperature between the internal and external junctions of:

$$W_i = Y_i \delta Q_i$$  \hspace{1cm} (3-A)

where $Y_i$ - the thermal conductance (Figure 2B)
Figure 2. Working Principle of Calorimeter
This small difference generates an electromagnetic force (i.e., e.m.f):

\[ e_i = S_i \delta Q_i \]  

(3-B)

where \( S_i \) - the thermo electric value of the thermocouple or

\[ e_i = \frac{S_i}{Y_i} W_i \]  

(3-C)

As all the thermocouples are connected in series, the total e.m.f is produced.

\[ E = \Sigma e_i \]  

(3-D)

where \( E \) corresponds to the power \( W \) transferred.

\[ E = \Sigma \left[ \frac{S_i}{Y_i} \right] W_i \]  

(3-E)

All the thermocouples are identical, they have the same thermal conductance and the same thermoelectric constant \( E \). Therefore:

\[ E = \left[ \frac{S}{Y} \right] \Sigma W_i \]  

(3-F)

\[ E = \left[ \frac{S}{Y} \right] W \]  

(3-G)

The electric signal is proportional to the power, \( A \) being the
calibration constant. Therefore:

\[ W = AE \quad (3-H) \]

As can be seen, the elementary temperature function does not appear in the resulting formula. If care is taken to prevent thermal losses by parasitic conductance of the thermocouples, the measurement is independent of temperature variations, either internal or external, and of the geometry of the thermal power "W". If this power "W" varies with time, the e.m.f signal varies proportionally. The construction of the fluxmeter is such that heat conductance, other than that due to the thermocouples, is negligible.

3.4.2.2 Variable Fluxmeter Measurement at Constant Temperature.
At the initial analysis, the experimental vessel and the fluxmeter can be respectively represented by a calorific capacity "M" and conductance "F" connecting the vessel to the calorimetric block at constant temperature \( Q_0 \). With "W" equals to the power generated in the vessel, "w" the power exchanged by fluxmeter and \( Q \) the temperature difference between the vessel and the heat block (Figure 2C), the system follows the equation:

\[ W = w + M \left[ \frac{\delta Q}{\delta t} \right] \quad \text{with} \quad Q = \frac{w}{F} \]

\[ W = \frac{w + M}{F} \left[ \frac{\delta w}{\delta t} \right] \quad (3-I) \]
The time constant of the system is $T = M/F$. As the thermal fluxmeter delivers a signal proportional to the exchanged power "w", the relationship between the power generated in the vessel and the electrical signal is:

$$W = A \{ E + T \left( \frac{\delta E}{\delta t} \right) \} \quad (3-J)$$

The constants "A" and "T" represent the static and dynamic calibration of the calorimeter. Dynamic calibration is rarely needed, although some experiments require more detailed analysis. The instrument's response to instantaneous power pulse and graded power is shown (Figure 2D & 2E).

3.4.2.3 Variable Temperature of Calorimetric Block Compensation through Symmetrical Increase. If the temperature $Q_0$ of the calorimetric block changes, either due to the residual instability of the regulator or to the temperature programming, the vessel follows the change and more towards $Q_0$. The heat flow measured by the fluxmeter, reflecting this change, can be represented by:

$$\left( \frac{M}{K} \right) \cdot \left( \frac{\delta Q_0}{\delta t} \right) \quad (3-K)$$

where $K$ - a constant representing the static calibration of the calorimeter
This variation in temperature requires thermal power which is transmitted by the fluxmeter. It produces an unexpected signal which can be greater than the signal produced by the experiment, especially in the programmed mode. To compensate for this incremental heat flow, a reference vessel is used. The signal from the reference vessel subtracted from the sample vessel reflects a net heat change due to the sample only. For optimum sensitivity, the heat capacity of the reference vessel should be the same as the net heat capacity of the sample vessel. Any difference in signal is then due to the heat capacity change of the sample, "ΔM". In a linear program this can be represented by:

$$\Delta M = \frac{K \Delta E}{\delta Q_0 / \delta t}$$ \hspace{1cm} (3-L)

or between two limits:

$$\Delta M = \frac{Q_0 + \Delta Q}{\Delta Q \int \Delta E \delta t}$$ \hspace{1cm} (3-M)

This is the technique used for making specific heat measurements. In order to obtain a good base line, the balance between the heat capacity of the reference vessel and the experimental vessel has to be established.

3.4.3 Design Aspects of the Instrument

The C-80 is symmetrical in design. A "reference" heat flux transducer is fitted electrically in opposition to the "measurement" transducer in such a way so as to cancel out the effect of residual deviation in calorimetric unit's temperature and
of outside electrical interference. This compensation is only effective if the experimental vessels fitted in the detectors are themselves symmetrical. However, the set-up could not begin to be identical as all the phenomena would then be cancelled out, even those under study. In general, the two mechanisms containing the samples are identical, but the samples are different. The reference vessel contains a non-reactive compound; or more rarely a compound whose reaction is known. In this case the known reaction can be used as a fixed "standard". The calorimeter then acts as a variance indicator from zero, and the reference transducer's sensitivity must be known (absolute and differential calibration of the fluxmeters). The quality of the compensation will be better as greater sensitivity in practice becomes involved. In order to improve quality, one can use a reference sample different from the experimental sample but with similar heat capacity or adjust the mass and physical characteristics of the reference experimentally to minimize the transient effects.

3.4.4 Thermal Equilibrium of the Vessels.

When a vessel is introduced into the calorimeter, a large heat flux is observed due to the initial difference in temperature between the vessel and block. This flux is attributed to the amount of heat transmitted changes the calorimetric block temperature which has neither infinite heat capacity nor an infinitely short response time. Through temperature control, the calorimeter block progressively returns to its initial temperature,
which produces a residual heat flux which is symmetrical for both transducers. However, it can be easily observed if measurement is made on only one transducer ("reference" transducer if the "measurement" vessel is introduced). In order to achieve accurate measurements, it is recommended to wait until equilibrium of the block is reached (normally 3 to 5 hours) before starting the calorimetric experiment, even if the differential signal is stable. There is no justification on experimental grounds for removing the reference vessel for each experiment, it is better to leave it in the calorimeter, rather than remove it systematically. Thus there is less variation in the block’s temperature. There are obvious advantages to initially prestabilize the vessel temperature with that of the block before its introduction, as this will result in the continuous stabilization of the unit throughout the entire experiment.

3.4.5 Instrument Lay-Out.

The complete set-up of the calorimeter is shown in Figure 3 with the basic units necessary for the measurements. Auxiliary components may be connected to the unit such as X-Y plotter, digital temperature, digital voltmeter and scientific calculator for acquisition and processing the data as well as for automatic remote control of the temperature programmer\(^{18}\).

The whole set-up consists of 1) Reversing Device; The unit is in the form of a vertical cylinder on rectangular base which rotates at an angle when activated. The fluxmeters are at the
center of the instrument, as well as in the experimental vessel; the measurement and reference vessel. 3) Temperature program module. This unit controls the temperature of the calibration vessel and a platinum probe on which is the transducer that provides power through transformer into the heating element. The programmer module generates a linearized electrical signal that amplifies the temperature input coming from the transducer, which will control the temperature. The control amplifier output is the trigger for the chart recorder. The unit has the capability to range from 10 mV to 100 mV. 4) Chart Recorder. The recorder is connected directly to the calorimeter and up to 1 mV, the measuring threshold is approximately 10 mV. The type of chart recorder used for the experiment is the Fisher Recordall Series 500 having two pairs for recording and input voltage range from 1 mV to 10 mV.

Figure 3. Instrument Set-Up
center of the instrument, as well as the two experimental vessels; the measurement and reference vessels. 2) Temperature Programmer/Controller; The unit controls the temperature of the calorimeter by means of a platinum probe on which is the transducer that drives the power through transformer into the heating elements. The programmer module generates a linearized electrical signal which follows the temperature program. It compares this signal with the one provided by the transducer and supplies a difference signal which will control the temperature. The controller module amplifies the different signal coming from the programmer and adds the corrective actions such as integral and derivative. The output signal that drives the heating and is also fed back to the controller in order to compensate the main voltage fluctuation. The unit has the temperature range from 0 to 300°C. 3) Amplifier; The amplifier is designed to amplify low DC voltage and has special characteristics of wide ranges, low noise, stability and dynamics suitable for use in conjunction with the calorimeter. The unit has the range of output signal from 10 μV to 10 mV. 4) Chart Recorder; The recorder is connected directly to the calorimeter and up to 1 mV, the measuring threshold is approximately 10 μW. The type of chart recorder used for the experiment is of Fisher Recordall Series 5000 having two pens for recording and input voltage range from 1 mV to 10 V.

3.4.6 Instrument Applications.

The C-80 calorimeter can be used as a thermodynamic research
tool to gather information about a substance or a transformation process; or it may be used to monitor a specific reaction or series of reactions; titration, process control, analysis, etc. Some typical applications of the instrument include the study of change of state or transitions in numerous materials, the measurements of the specific heats of solids and liquids, characterization of materials as to their storage capacity and the temperature range over which the transformation occurs, determination of thermal stability of products, the study of adsorption of a vapor phase on a solid sample, measurement of heat of dissolution and heat of hydration, wetting characteristics of any material (hydrophobic or hydrophilic) with respect to a particular liquid, and selection of microbial activity.

In this research work, the calorimeter will be primarily utilized to measure the heat of wetting using the reversing mechanism. The complete description of the vessel’s internal segments are shown in Figure 4. In the case of liquid/solid system, the reference vessel will use the same liquid as the sample vessel while maintaining the same dead volumes in both. As the liquid and solid contact is achieved, the heat is generated inside the vessel which corresponds to the power, W. The mixing is done by activating the reversing device of the calorimeter. It will be returned to the original upright position as soon as the mixing is complete. The small heat liberated is converted into signal which in turn is fed into the chart recorder. The total heat is determined by integrating the area under the curve and multiplying
Figure 4. Mixing Cell Showing Internal Segments
by the sensitivity constant of the calorimeter.
4.0 SURFACE AREA DETERMINATION

4.1 Surface Area of a Solid

The surface area determination can be made by adsorption studies. The problem in defining the surface area is similar to the difficulty in measuring the length of coastline of California. The length of any coastline in the world can not be easily represented by a simple straight line. The fact that irregularities due to bays, harbors would undoubtedly increase its length. The same situation is confronted in the case of measuring the surface area of a solid. The Heisenberge principle would inform us that there is considerable uncertainty in the location of electrons and that the surface area of an atom is a philosophical concept. One could, however, determine the coastal villages or landing jetties and take this number as a measure of the length of a stretch of coast. Alternatively, one could also refuse to consider the irregularities smaller than some specified size. Indeed, the coastline length turns out to be an elusive notion that slips between the fingers of one who grasps it. In the case of a solid surface, it is possible that a method of counting the number of atoms or molecules on the surface be applied which will produce a useful measurement of surface area of no absolute value. Another difficulty that needs to be considered in surface area determination is that atoms and molecules on the surface possess different properties from one location to another thus
yielding surface heterogeneity. In cases where adsorption depends on surface energy quantities or on interatomic spacings, the amounts of material adsorbed on hypothetical samples of solid of the same total area may be quite different. In such a situation, even the relative amounts adsorbed on the different samples would not be a unique measure of the relative areas. The surface area estimation by adsorption studies can predict the behavior of adsorbates better than the variation of the relative heat of immersion or the relative microscopic areas.

4.2 Methods of Determination

4.2.1 Liquid/Solid System

Ritter and Drake\(^{(41)}\) utilized mercury for the determination of porosity of solids which later known as mercury porosimeter. This method does not determine the surface area directly but rather the pore size distribution in a porous material. The solid sample was placed in a long-necked sample bulb, and the entire dilatometer was filled with mercury and placed in a protective bomb of 60,000 psi nitrogen pressure. As pressure was applied, mercury penetrated into the pores of the solid, and an increasing length of resistance wire was exposed in the neck of the dilatometer. The volume penetrated could then be calculated by measuring the resistance of the wire.

In some cases, the surface area of a solid can be determined provided other thermodynamic quantity such as heat of solution of
a powder, its solubility increase or its heat of immersion is known. Bartell and Fu\textsuperscript{(47)}, for instance, claimed that the heat of immersion of a powder is related to the surface area by the following equation:

\[ q_{\text{imm}} = A_s (E_{sv} - E_{sl}) \]  

(4-A)

where  
\( q_{\text{imm}} \) - heat of immersion on a per gram basis  
\( A_s \) - the area of solid per gram  
\( E_{sv} \) - surface free energy of solid and liquid per unit area  
\( E_{sl} \) - surface free energy of solid and air per unit area

The area, \( A_s \), was obtained by combining the heat of immersion with data on the temperature dependence of the contact angle for the liquid. The \( q_{\text{imm}} \) was determined experimentally while \( (E_{sv} - E_{sl}) \) was estimated from the adsorption data or from the isosteric heat of adsorption.

Cooper\textsuperscript{(43)} studied and investigated a rather different approach to determine the surface area of solid. His method was based on the rate of dissolving of a soluble material (i.e., rock salt) at any given temperature, which was to be directly proportional to the surface area. The area estimated by this method did include a layer of film developed on the solid of a few microns thick but did not take into considerations the microscopic roughness of the
solid’s surface.

4.2.2 Gas/Solid System

There are a number of methods for the determination of the surface area of a solid available today. One of such methods is that using gas chromatography originated and developed by Nelson and Eggertsen\(^\text{(44)}\). The technique employs the mechanism of adsorbing the adsorbate gas from a flowing mixture of adsorbate and an inert non-adsorbable carrier gas onto the solid. The change in the thermal conductivity of the gas mixture is measured and used as a means to monitor the process of adsorption and desorption. The adsorption is initiated as the sample contained in a cell is immersed in an appropriate coolant. The commonly used coolant is liquid nitrogen. It is the adsorbate in a helium carrier. The change in the thermal conductivity of the gas mixture produces an adsorption peak indicating the decrease in adsorbate concentration due to adsorption on the solid surface. The adsorption is said to be completed when there is no changes in the thermal conductivities between the gas entering and leaving the sample cell. The desorption process begins as soon as the sample cell is removed from the coolant. The gas leaving the cell is now rich in adsorbate concentration and the signal that is being generated will ideally be in the opposite in polarity to that of the adsorption. The solid surface is covered by the monolayer of adsorbate and the surface area can be easily calculated using the cross-sectional area of the adsorbate molecules. The measurements can be
interpreted by means of BET theory. The Kozeny-Carman equation is known to be able to calculate an average particle size, or to estimate the surface area of the powder. The technique called permeability method is based on the calculation of Kozeny-Carman equation which in fact is theoretically independent of the absolute porosity of the powder plug on which the measurements are made. The most attractive feature of permeability technique lies in its simplicity in terms of equipment involved. The use of a large sample of powder is permissible and so sampling problems are minimized. In order to differentiate primary particles, agglomerates and aggregates, complete particle characterizations have to include a study of the particle structure. Palik has described the complete structure characterization of powders utilizing a combination of two or three of the following techniques: particle sizing, gas adsorption surface area measurement (BET) and scanning electron microscopre (SEM). The fluorescent materials coated with a secondary phase were used for the particulate characterization study. The large increase in the specific surface area of the sample was observed using the monosorb surface area analyzer when coating material was added. The observation led to the suggestion to use the BET measurements to monitor the addition of a fine phase to a surface.

The use of the electron microscope had been tried by Bowden and Rideal to determine the surface area of a platinized platinum electrode. The basic concept behind the method was that the rate of charging of a polarized electrode surface could give relative
areas. Joncich and Hackerman\textsuperscript{67} conducted similar experiments and found that the areas for platinized platinum were in good agreement with those given by the BET gas adsorption method.

Frequently, the adsorption and desorption isotherms are not the same due to extensive pore structure found in many powder samples. Normally porous materials exhibit hysteresis (Figure 5) and the desorption isotherm is usually used if pore size distributions are to be determined. Below the critical temperature of the adsorbate, adsorption is generally multilayer in type, and the presence of pores may have the effect in limiting the possible number of layers of adsorbate as well as introducing the capillary condensation phenomena\textsuperscript{48}. In general, most of the isotherms may tend to flatten as $P/P_0$ (i.e. relative pressure) approaches unity. The closed type shape of hysteresis loop in (Figure 5) can be explained in terms of capillary condensation. Zsigmondy\textsuperscript{49} attributed hysteresis to contact angle hysteresis due to impurities.

4.2.3 Small Surface Area Measurements

Surface areas as low as 0.1 m\textsuperscript{2}/g can be determined by the continuous flow method\textsuperscript{50}. A problem, however, sometimes arises from the fact that thermal diffusion signals may merge together with the adsorption and desorption signals which results in the deviations of true low surface area measurements. The thermal diffusion signals are caused by the separation of mixed gases, which occurs when the temperature gradient is changing. They
appear as shoulders on the adsorption and desorption signals. However, this phenomenon ceases to exist when a steady-state gradient is established. The elimination of thermal diffusion can be achieved by means of increasing the linear gas flow velocity through the sample cell and decreasing the void volume in the cell. The accomplishment of such a technique is through the use of proper cell geometry as discussed by Lowell and Karp\(^{51}\). They measured surface areas as low as \(0.01 \text{ m}^2 / \text{g}\) in the cell using either U-shaped micro cell for small samples or a capillary cell for large quantities of low surface area materials. The thermal gradient that caused the thermal diffusion, originates in the arms of a sample cell immersed in liquid resulting in a transitory separation of a gas mixture flowing through the cell. Benson\(^{52}\) postulated the coefficient of thermal diffusion \(D_f\), as being given by:

\[
D_f = \frac{N' - N''}{N_t} \frac{1}{\ln (T_1/T_2)}
\]

where

- \(N'\) = adsorbate concentration at higher temperature \(T_2\)
- \(N''\) = adsorbate concentration at lower temperature \(T_1\)
- \(N_t\) = total molecular concentration of adsorbate and carrier gas
Figure 5. Typical Adsorption-Desorption Isotherm Showing Hysteresis
Another method of eliminating the effect of thermal diffusion is by the use of krypton-helium mixture. The krypton exhibits low vapor pressure at liquid nitrogen temperature thus ceasing the existence of the thermal diffusion phenomenon.
5.0 THEORETICAL CONCEPTS

In the following sections, the theories and concepts of contact angle and spreading coefficient, mechanism of adsorption, the surface energy of solids and heat of immersion, BET isotherms, and flotation will be discussed.

5.1 Fundamental of Wetting

In an attempt to measure the heat of immersion of a solid in a certain liquid, one can not ignore the question of the phenomena occurring between these two phases. It is commonly known that drops of water on an inclined solid surface can remain stationary, or can move under gravity. If water is placed on wax paper, the thin sheet of water formed initially will break up into beads. Two types of behavior are observed on a given solid surface, one where the liquid forms beads and the other where it forms a film. It is easy to assume that the liquids which have strong affinities for a solid will form films such that the liquid-solid contact is maximized while those which have weaker affinities will collect themselves into beads. The above affinity is referred to as the wettability. Also, the wetting is sometimes interpreted as the phenomenon where the contact angle between a liquid and a solid is zero or so close to zero that the liquid spreads over the solid easily, and that non-wetting means that the angle is greater than 90° so the liquid tends to form beads and run off the surface.
5.1.1 Contact Angle and Spreading Coefficient

Since the configurations of a wetting liquid and a non-wetting liquid on a solid surface differ substantially in their interfacial areas, any quantitative description of wettability must involve the interfacial energies in a major way. The surface tensions between solid-liquid (sl), solid-vapor (sv) and liquid-vapor (lv) are expressed in Young's equation:

\[ Y_{lv} \cos \lambda = Y_{sv} - Y_{sl} \]  \hspace{0.5cm} (5-A)

where

- \( Y_{lv} \) - surface tension or surface free energy of liquid and vapor
- \( Y_{sv} \) - surface free energy of solid and vapor
- \( Y_{sl} \) - surface free energy of solid and liquid
- \( \lambda \) - contact angle

Young's equation has certain basic limitations that it is only valid where there is no adsorption at the interfaces and the interfacial tensions that appear in the equation are those which are evaluated far from the contact line. The interfacial tensions at the contact line may have different values, however, and indeed may not be well defined owing to the overlap of the portions of three interfacial regions. All such deviations near the contact line can be summed up together in the form of the additional effect.
of line tension. It is noteworthy that the measure values of line tension show that they are extremely small. Thus the contact angle that is predicted by Young’s equation is quite likely the one that is measured.

The interfacial or surface tensions are equilibrium properties as well as the contact angle, \( \lambda \). Consequently, \( \lambda \) is referred to as the equilibrium contact angle. For practical purposes, it is safe to state that if the contact angle is greater than 90°, the liquid is unlikely to wet the solid. On the other hand, a liquid is considered to wet a solid only if the contact angle is zero.

The free energy change is utilized for the spreading of a film of liquid over the solid and is called the spreading coefficient which is defined as:

\[
S_u = Y_{lv} - Y_{lv} - Y_d
\]  

(5-B)

where \( S_u \) – spreading coefficient of liquid over solid

The positive value of \( S_u \) is attributed to the spreading which is accompanied by a decrease in free energy and by wetting of liquid.

For a non-wetting liquid situation, one finds on substitution equation (5-A) into (5-B) that

\[
S_u = Y_{lv} \left( \cos \lambda - 1 \right)
\]  

(5-C)

Thus the spreading coefficient is negative. The knowledge of
interfacial tensions alone is known to be sufficient to predict the wettability of a liquid on a solid surface using equation (5-B). The spreading phenomenon of liquid over solid very much resembles duplex (thick film) and non-duplex spreading in liquid-liquid systems. The formation of an initial layer of film on the solid by the liquid is primarily observed. This is also seen when liquid A spreads onto liquid B when the spreading coefficient is positive. Generally speaking, this happens when a liquid of low surface tension is placed on one of high surface tension. Conversely, a liquid of high surface tension would not spread on one of much lower surface tension, so the spreading coefficient is negative.

The discussions presented above assume that both of the liquids are pure. However, when two substances are in contact, they will become mutually saturated. In the case of benzene and water, for instance, the lower surface tension liquid will have a positive initial spreading coefficient and so a rapid initial spreading occurs. The mutual saturation takes place, the benzene retracts to a lens formation and the water surface left behind is no longer pure. The final negative surface coefficient comes about because the film pressure of the Gibbs monolayer is large enough to reduce the surface tension of the benzene-water interface to a value below the sum of the other two. Thus, equilibrium seems to be that of a monolayer with any excess liquid collected as a lens.

Spread wetting occurs with liquids on solids of high free surface energy. The spreading of a liquid into a stable, multimolecular film on the solid has been observed most often and
is analogous to the initial duplex spreading of a liquid into a multimolecular film on another liquid. Such a film on liquids is not stable, however, and reverts to a monolayer and lens for the numerous systems. Nonduplex spreading of a liquid into a monolayer on another liquid has its counterpart in liquid-solid systems, where an adsorbed, oriented, and close-packed monolayer is formed upon which the liquid can not spread.

5.2 Mechanism of Adsorption

5.2.1 Adsorption of Liquids on Solids

The adsorption of solution by solids is of great practical importance and a vast number of papers have been published, thus, a fundamental understanding has been developed. The role of the solvent and its competition with the solute for surface sites has now become recognized as an important factor, particularly as a result of a large number of studies on the adsorption from binary liquid mixtures and their thermodynamic analysis. Most adsorbents are heterogenous in the surface chemical sense in that they contain a wide range of high to low energy sites, both polar and non-polar, as well as impurity atoms and adsorbed material (e.g. moisture and organic contaminants arising from exposure to the environment). The interaction between the surface and adsorbed species may be either chemical or physical. Several types of bonding can be identified as 1) chemical adsorption (chemisorption), 2) hydrogen bonding 3) hydrophobic bonding and 4) van der Waals forces. The
net interaction of an adsorbate molecule with a surface might involve more than one type of interaction, depending on the chemical structure of both components. The most favored approach to an investigation of the adsorption mechanism is a study of the isotherm. It is not only the most convenient form in which to obtain and plot experimental data, but it is also the form in which theoretical treatment are most easily developed.

5.2.2 Adsorption of Gases on Solids

In many cases where adsorption is used for practical purposes, the adsorption takes place from flowing gases. Differing from static adsorption, which takes place in a closed system, adsorption from flowing media is called dynamic adsorption. The molecule of an adsorbing gas is carried by an enforced gas flow and by diffusion in the direction of pressure and concentration gradients. When a gas stream flows around an adsorbent particle, a thin layer adheres to the particle surface—a film which is practically immobile. The concentration of the adsorbing gas is less in this film during adsorption than in the middle of the gas stream. External diffusion through the adhering film is taking place which is, at times, referred to as mass transfer. In the case where the adsorbent particle is porous, adsorption on the inner surface is preceded by mass transport through the pores (i.e., internal diffusion). The diffusion outside the adsorbent particles may also take place (i.e., external diffusion) in the direction to the bulk gas flow.
5.3 Surface Energy of Solids and Heat of Immersion

The surface energy, or, more precisely, surface free energy, is one of the most important parameters in determining the adsorptive and wetting characteristics of a solid in the presence of vapor or liquid. They subsequently influence the flocculation, aggregation, crystal growth, and most other colloidal behavior exhibited by solid particles. The surface energy values can be determined from the measurements of differences in the heats of solution of finely divided particles and large crystals of a substance. These measurements, however, are difficult to obtain, owing to the difficulty of assessment in the strain imparted to a solid as particle size is decreased and effects due to surface lattice imperfections. It is generally known fact that when a clean solid is immersed in a liquid, heat will be liberated, and this heat of immersion may be written as:

\[ q_{\text{imm}} = E_s - E_{sl} \]  \hspace{1cm} (5-D)

where

- \( E_s \) - surface energy of solid per unit area
- \( E_{sl} \) - surface energy of solid and liquid interface per unit area
- \( q_{\text{imm}} \) - heat of immersion of solid per unit area

The exothermic or endothermic heat of immersion having its small
value is usually expressed on a per unit area basis with the exception of porous solids or agglomerates of small particles where capillary condensation can occur between primary particles. One can also define an energy of adhesion, analogous to the work of adhesion which is the work necessary to separate the liquid and adsorbed vapor from the solid surfaces.

$$E_{A(0)} = W_d - T \frac{\delta W_d}{\delta T} = E_s + E_l - E_d$$  \hspace{1cm} (5-E)

where
- $E_{A(0)}$ - surface energy of a solid A at solid-liquid interface per unit area
- $W_d$ - work of adhesion at solid interface per unit area
- $E_s$ - surface energy of liquid per unit area
- $T$ - operating temperature

A polar solid will exhibit a large heat of immersion in a polar liquid and a smaller one in a non-polar liquid; the non-polar solids, such as graphon or teflon, have a low heat of immersion with little dependence on the nature of the solid. The finding of some researchers is that the $q_{imm}$ of a given solid is essentially a linear function of the dipole moment of the wetting liquid. The difference in the heat of immersion of a clean surface and with the one of a preadsorbed film of the same fluid can be related to the heat of adsorption of the film. There is always the phenomenon of adsorption occurring at the solid-gas interface and
the amount of adsorption can be significant and may approach or exceed the point of monolayer formation. This type of adsorption is generally referred to as physical adsorption and the forces responsible are of the van der Waals type. The adsorption data may be employed to determine changes in the solid-gas interfacial free energy. The typical adsorption isotherm is that of a plot of the amount adsorbed expressed as cubic centimeters at Standard Temperature and Pressure (i.e., STP) per gram of solid versus \( \frac{P}{P_0} \), where \( P \) is the actual pressure of the gas and \( P_0 \) is its saturation pressure (i.e., vapor pressure of pure liquid adsorbate). Using the Gibbs equation, the relationship is written as:

\[
\delta Y = -\Gamma R T \delta \ln a
\]  

(5-F)

where

- \( R \) — gas constant
- \( T \) — operating temperature
- \( \Gamma \) — surface excess per square centimeter
- \( a \) — the activity
- \( Y \) — surface free energy or surface tension

For an ideal gas, the activity can be replaced by the pressure, and

\[
\delta Y = -\Gamma R T \delta \ln P
\]  

(5-G)

or

\[
\Pi = - \int \delta Y = R T \int \Gamma \delta \ln P
\]  

(5-H)
Also, 

\[ \Pi = Y_s - Y_{sv} = \frac{RT}{\Sigma} \int n \, \delta \ln P \]  

(5-I)

\[ \Pi^0 = Y_i - Y_{i,v} = \frac{RT}{\Sigma} \int n \, \delta \ln P \]  

(5-J)

where 
- \( \Pi \) - the film pressure
- \( \Sigma \) - specific surface area
- \( n \) - moles adsorbed per gram

The equations (5-I) and (5-J) both provide a thermodynamic evaluation of the change in interfacial free energy accompanying adsorption. The adsorption isotherms are usually reversible in that adsorption and desorption curve are identical. Most solids exhibit heterogenous surface and so \( Y_s \) and \( Y_{sv} \) are not well defined as separate quantities. The heat of immersion of a clean solid \( q_{imm} \), can be referred to as the immersion of a solid having an adsorbed film on the surface. The \( q_{sv,imm} \) on the other hand, is the heat of immersion of solid with adsorbed film in the liquid adsorbate. Both quantities are related by the expression:

\[ q_{s,imm} - q_{sv,imm} = \Pi - T \frac{\delta \Pi}{\delta T} + \Gamma' \Delta H_v \]  

(5-K)

where 
- \( \Gamma' \) - number of mole adsorbed per unit surface area
- \( \Delta H_v \) - molar enthalpy of vaporization of the liquid adsorbate
The heat of immersion can also be related to the contact angle. By differentiation of equation (5-A), one can have:

\[ q_{\text{imm}} = E_v - E_d = E_n \cos \lambda - \frac{T V \delta \cos \lambda}{\delta T} \]  

(5-L)

The equation (5-L) can be evaluated by measuring the heat of immersion and contact angle experimentally and it can be utilized for a test of the thermodynamic status of Young's equation.

Clint\textsuperscript{(33)} obtained the equation for heat of immersion taking into consideration the clean and precoated with adsorbate, and the isosteric enthalpy of adsorption at surface coverage:

\[ q_{s,\text{imm}} - q_{s,\text{imm}} = \frac{1}{A} \int_{0}^{n_0} q_s \delta n_s - \frac{1}{A} \Delta H_v \]

\[ q_{s,\text{imm}} - q_{s,\text{imm}} = \frac{1}{A} \int_{0}^{n_0} (q_s - \Delta H_v) \delta n_s \]  

(5-M)

where

- \( A \) - the specific surface area of the solid
- \( q_s \) - isosteric enthalpy of adsorption at a surface coverage
- \( n_s \) - the surface coverage

Assuming that the enthalpy of immersion of the solid, preequilibrated with the saturated vapor, is equal to the total enthalpy of the liquid surface \( (q_n) \), then
Subtracting equation (5-M) from equation (5-N) gives:

\[ q_{sv} = \frac{1}{A} \int_{0}^{\infty} (q_{st} - \Delta H_{v}) \delta n_{s} + q_{lv} \]  \hspace{1cm} (5-O)

or the heat of immersion per gram of solid is:

\[ \Delta q_{imm} = A q_{sv} = \int_{0}^{\infty} (q_{st} - \Delta H_{v}) \delta n_{s} + A q_{lv} \]  \hspace{1cm} (5-P)

The equations (5-N) and (5-P) enable the heat of immersion of a solid in a liquid as a function of precoverage of adsorbed vapor to be predicted from data of the isosteric enthalpy of adsorption as a function of coverage together with a value for the enthalpy of the liquid surface.

Everett\(^{(54)}\) obtained an empirical relation between the heat of immersion and \((T - T_{f})\); where \(T_{f}\) is the melting point of the \(n\)-alkane.

\[ \log_{10}[(\Delta q_{imm}) - 120.0] = 2.129 - 1.630 \times 10^{12} (T - T_{f}) \]  \hspace{1cm} (5-Q)

The equation (5-D) had no significant contributions to \(\Delta q_{imm}\) values from various types of hydrocarbon interactions. However, he noted that pure \(n\)-alkane liquid on the surface adjacent to a graphitized carbon surface possessed the properties of the bulk solid at
temperatures close to the melting point.

5.4 BET Isotherms

Brunauer\(^{55}\) classified isotherms in five basic types as shown in Figure 6. Type I is the Langmuir type, roughly characterized by a monotonic approach to a limiting adsorption that corresponds to a complete monolayer. Type II is very common in the case of physical adsorption and corresponds to multilayer formation. The point B of the type II is commonly taken as the point where the complete of monolayer has taken place. Unlike the above two types of isotherms, type III is very rare and characterized by a heat of adsorption equal to or less than the heat of liquefication of the adsorbate. Type IV and V are considered to reflect the capillary condensation phenomenon in that they level off before the saturation pressure is reached and may show hysteresis effects. The BET isotherm usually applies in the range of 0.7-1.3 layers. When measurements are carried out in the vicinity of the boiling point of the adsorbed gas, the range of validity of the BET theory, expressed in terms of the relative pressure, will vary from 0.05 to 0.35. In the case of measurements carried out at lower temperatures, especially below the melting point of the adsorbate, the validity range shifts towards lower relative pressures - for example, with krypton at 77 K the BET theory generally applies for relative pressures range 0.005-0.150. At low pressures, the extent of the adsorption predicted by the BET theory is usually less...
Figure 6. Brunauer's Adsorption Isotherms
than that determined experimentally, since the surface usually contains sites of a higher heat of adsorption than those which are occupied at monolayer surface coverage. After the most active sites have been covered, the properties of the rest of the surface are close to those of a homogenous surface. In type II and III, the curves approach \( P_0 \) line asymptotically; such behavior is observed for adsorption on powdered samples, and the approach toward infinite film thickness is due to the interparticle condensation. Type IV and V specifically refer to porous solids.

The BET equation can be represented by:

\[
\frac{x}{1 - x} = \frac{1}{C X_m} + \frac{(C - 1) x}{C X_m} \quad (5-R)
\]

where\(\frac{X}{1 - x}\), the ratio of partial pressure adsorbate to saturated vapor pressure of adsorbate

\(X_m\) - weight of adsorbate adsorbed at a monolayer coverage or mole per gram adsorbed at monolayer point

\(C\) - constant which is a function of the adsorbate condensation and heat of adsorption

\(x\) - weight of adsorbate adsorbed at relative pressure \(P/P_0\).
\( X_m \) and \( C \) can be obtained from the slope and intercept of the straight line best fitting the plot of \([x/X(1-x)]\) versus \(x\). The specific surface area can be evaluated from:

\[
X_m = \frac{\Sigma}{N \sigma}
\]  
(5-S)

where

- \( \Sigma \) - the specific surface area
- \( N \) - Avogadro's number
- \( \sigma \) - the area of a site

If the value of \( \sigma \) is known. In the case of multilayer adsorption, is considered as an adsorbate area, based on either solid or the liquid density.

5.4.1 Hysteresis

Normally, the adsorbates above their critical temperature do not produce multilayer type isotherms. Below the critical temperature, however, multilayer formation is possible and capillary condensation may occur. A wide range of porous adsorbants is now involved and usually having a broad distribution of pore sizes and shapes. The most general characteristic of such adsorption system is that of hysteresis as illustrated in Figure 5. The desorption branch lies to the left of the adsorption branch and the isotherms may tend to flatten as \(P/P_0\) approaches unity. The irreversibility of the adsorption-desorption process is caused by differences in the mechanisms of filling and emptying pores of specific shapes and sizes. The two theories most widely used to
explain the origin of this hysteresis are the open pore theory and the ink-bottle theory. In the open pore theory, pores are assumed to take the shape of regular capillaries open at both ends and never crossing one another. Capillary condensation may only take place when the pressure in the gas phase has increased to such a degree that the multimolecular adsorbed layers have merged to form a cylindrical condensate meniscus along the pore circumference. The relative pressure value can be determined by the radius of the meniscus along the pore circumference once the entire pore is filled. The theory of the ink-bottle shaped pores assumes that pores take the shape of cavities with one or several narrow inlet necks. With rising relative pressure, the bottle-shaped pores are filled with no delay, depending on the radius of curvature of the menisci formed. On decreasing the relative pressure, however, the pores are emptied only when the relative pressure decreases to a value which permits the condensate to evaporate from the menisci in the narrow necks.

5.5 Flotation

A very important but rather complex application of surface chemistry is to the separation of various types of solid particles from each other by what is known as flotation. The method is of enormous importance to mining industry as it permits large scale and economic processing of crushed ores whereby the desired mineral is separated from the nonmineral-containing material or gangue. A
list of ores would include calcite, fluorite, barite, silica and silicates, coal, graphite, sulfur, and soluble salts such as sylvite (potassium chloride).

The application of oil flotation was dated back in 1920 for the purpose of improving the mineral contents of copper and lead-zinc ore pulps by treatment with a large amount of fatty and oily mineral. Since then the procedure has been displaced by what is known as froth flotation. Froth flotation is by far the dominant process of mineral dressing in use today and its application includes the treatment of metallic ores that are generally ground finer than 48 (i.e., 297 micron) to 65 (i.e., 210 micron) mesh, or coal and certain non-metallics that are finer than 10 (i.e., 1.68 mm) to 28 (i.e., 595 micron) mesh. Some chemical additives such as collectors, which adsorbs on the mineral particles to make the basic modification in contact angle that is desired and frothing agents for promoting foam formation, are commonly incorporated in the froth flotation.

5.5.1 Flotation Experiment on Coal

Although coal exhibits natural floatability, its response to flotation varies with carbon content as shown in Figure 7.

Gaudin observed that the greater the ash content of a coal, the less hydrophobic is the coal. Most of the ash constituents of coal consist principally of silicates. Since silicates are readily wetted by water, the reduction of natural hydrophobicity with increasing ash content would be expected.
Figure 7. Variation of Contact Angle with Carbon Content of Coal
Sulfur content of coal is of considerable importance from an environmental standpoint. The organic sulfur is incorporated structurally in the macromolecular coal polymer as thiophenes, sulfur ring structures, which cannot be separated by flotation techniques. The inorganic sulfur is present largely as ferrous disulfide in the form of pyrite and marcasite.

In the flotation experiments, MIBC and kerosene are commonly used as frother and collector agent. The kerosene is used to mask hydrophilic sites arising from the heterogenous nature of the solid. With this flotation strategy, a major portion ($\approx 85\%$) of the feed material can be recovered in the concentrate. The kerosene collector used in this research experiments encourages the contact between the coal particles and air bubbles. The contact is made by the formation of a thin coating over the particle to be floated. That is to say that the collector provides hydrophobicity to the mineral surface as a result of collector adsorption. The MIBC frother is used to generate bubbles in the flotation cell. Once formed, they tend to rise in the liquid under the effect of buoyancy.

An alternative flotation strategy has been proposed by Miller.$^{58}$ This two-stage process for desulfurization involves flotation of pyrite from the depressed coal. The first stage is conventional flotation, while the second stage involves conditioning the first stage concentrate with a dextrin-type depressant and a sulfhydryl collector. The pyrite is floated from the coal in the second stage.
6.0 EXPERIMENTAL TECHNIQUE

6.1 Materials and Reagents

The materials and reagents involved in the heat of immersion and flotation experiments will be discussed in the following sections.

6.1.1 Coal

The type of coal that was used was bituminous, high volatile A Pittsburgh seam coal supplied by Pittsburgh Energy Technology Center, U.S. Department of Energy. The moisture and ash content, and the ultimate analysis of the as received coal are given in Table A-3. The coal sample was dry screened on a ro-tap to the desired size range and the analysis of the screening is presented in Table A-4. The coal samples of different particle sizes were initially dried in argon circulating oven at 313 K for four days to ensure the absence of oxidation on the surface. The sample was re-dried in the argon circulating oven for 10 minutes after every heat of immersion conducted.

6.1.2 Water

The immersional fluid used in the heat of immersion experiments is water. The water was distilled and de-ionized prior to its usage.
6.1.3 Methanol

The other immersional fluid utilized in this research work is anhydrous methanol purchased from Fisher Scientific Company having 99.90% purity (Karl Fischer Grade), acetone free and suitable for microscopic work.

6.1.4 Flotation Agents

In the flotation experiments, flotation agents such as MIBC (i.e., frother agent) and Kerosene (i.e., collector agent) in water were incorporated. The coal sample having 200 gm in weight in 4000 ml of water was mixed with 60 μl of MIBC (i.e., 0.5 lb of MIBC/ton of coal) and 360 μl of Kerosene (i.e., 3.0 lb of Kerosene/ton of coal).

6.1.4.1 MIBC. This floating agent has a chemical name of methyl isobutyl carbinol and has a molecular weight of 102 mass units per mole. It has an empirical formula of C₆H₁₃OH and is supplied by Aldrich Chemical Company.

6.1.4.2 Kerosene. The use of Kerosene as collector agent is very well-known in flotation experiments. Most of collectors are heterogeneous compounds that contain a functional inorganic group coupled with a hydrocarbon chain. The collector provides coal which is to be floated with a water-repellent air-avid coating that will adhere to an air bubble. The kerosene used was manufactured by Fisher Scientific Company.
6.2 Calorimeter Experiments

6.2.1 Operational Procedure

The operation of Setaram C-80 Heat-Flux microcalorimeter requires a constant temperature environment due to the fact that it is very sensitive instrument to temperature changes. So the laboratory where the experiments were conducted has to be equipped with minimal circulation of hot and/or cool air.

The operation in switching on and off the modules has to be performed in sequence so as to prevent any surges in the controller. It is a good practice to turn on the switches from right to left and vice versa when shutting down the instrument. The temperature reading will be displayed on the programmer showing the lower temperature limit. At the start of the operation, the balance meter will indicate some negative value which means that the calorimeter is warmer than the temperature set by the programmer. A scan rate of 2.0°C/min is set and the heating button on the programmer is depressed. As soon as the balance meter indicates "0", the isothermal button is depressed. The clear button on the temperature controller is then pushed once. The temperature controller is a PID (i.e., proportional, integral, derivative) device. The proportional switch is set at 5 while both the integral and derivative switch are set at 1 throughout the entire operation of the calorimeter. In order to set the balance meter in the amplifier to zero, the coarse zero and fine zero adjustment knobs are used together with polarity setting knob.
There are 3 switching positions on the polarity setting knob to define the polarity of the offset voltage ("-", "0", "+"). The range switch is moved to the most sensitive setting (i.e., 10 microvolts). The coarse as well as fine adjustment knob are turned in clockwise and anti-clockwise direction until the zero reading on the balance meter is displayed.

6.2.2 Calibration Material

The chemical reagent used in order to calibrate the calorimeter is potassium chloride (KCl) obtained from National Bureau of Standards (Standard Reference Material No.1655 for solution calorimetry). The heat of dissolution of potassium chloride was measured for the purpose.

6.2.3 Calibrating the Calorimeter

The actual heat of immersion experiments incorporates the use of the stainless steel reversing (mixing) vessels as does the calibration procedure using potassium chloride. The main function of the vessels is to mix the two components; a solid and a liquid phase. A layer of mercury having volume of 600 - 800 µl is discharged from a micropipett into the small internal sample vessel. Mercury is used to prevent the coal sample from adhering to the wall of the vessel. The coal sample weighing 30-50 mg is added on top of the mercury. The internal vessel is closed with a small stainless steel cap fabricated solely for this purpose. The main mixing cell body is connected to the internal cell and is
screwed down tightly. Another layer of mercury of 800-1200 µl is introduced into the main cell body to seal off the possible opening created by the stainless steel cap and the internal vessel. It also serves as a barrier to prevent mixing of coal sample with the immersional fluid prior to the initiation of the experiment. The amount of immersional fluid used is approximately 4-5 ml which is placed on top of the liquid mercury. The introduction of the immersional fluid will minimize the air space available in the mixing cell body. The same procedure is used for the reference cell except that the coal sample is omitted. Both vessels are put carefully in the openings of calorimeter and held down securely by the threaded stainless steel caps. The whole assembly is left for about 3-4 hours in order to reach thermal equilibrium. It is important to note that in both vessels, the amount of mercury and immersional fluid used have to be identical. This will increase the sensitivity of the heat-flux calorimeter. It is recommended, however, that the removal of the reference vessel for each experiment is not required. This will lessen the perturbation of the temperature of the calorimetric block to some extent so that rapid stabilization can be achieved more quickly. Stabilization is indicated by balance meter in the amplifier showing "0" and the experiment can be initiated. The amplification of the signal from calorimetric measurement is done by selecting appropriate voltage range from 10 µV - 10 mV of the amplifier. This electrical signal originated from the conversion of heat of generation of the experiment is fed to the chart recorder. The acquisition of
Experimental data is started by activating the reversing mechanism that inverts the cylindrical part of the calorimetric assembly at an angle of about 180°.

Typically, the reversing is continued for 20-30 minutes for the coal samples. For more miscible samples, the shorter time of inverting operation was required. In order to insure reproducibility of results, it is desired to have the same inverting operation time or the same number of inversions for each experiment. The signal/balance meter will return to "0" indicating that all of heat has been released or absorbed and the calorimeter is back to equilibrium.

The signal generated by the calorimeter as a result of heat being released or absorbed is displayed on the chart paper and its area is integrated and multiplied by the sensitivity constant obtained from Figure 8. The evaluation of the area under the curve will in turn determine the total heat released or adsorbed. The typical curve for calibration of calorimeter using the heat of dissolution of potassium chloride at 303 K is shown Figure 9.

6.2.4 Mercury Cleaning

The liquid mercury used in each experiment had to be cleaned thoroughly prior to further usage. Precautions are taken in handling the mercury as its vapor poses a great health risk to humans so the process of pouring the mercury from the mixing cell body to a glass beaker as well as withdrawing it from the container using the micropipette have to be done under a chemical hood.
The cleaning procedure is performed when about six pounds of used mercury are collected in the beaker. The removal of contaminant on the mercury is achieved with the addition of 1/20 N solution of nitric acid (i.e., 33 ml of HNO₃ in 1000 ml of water). The mixture is left for twenty four hours while occasionally stirring with a glass rod. The mercury will gradually show its brilliant shine indicating that the contaminant has been removed and it is then ready to be rinsed with water. Flowing water from the tap is allowed to pour into the beaker containing the mercury and acid solution. Another beaker is also introduced big enough to surround the beaker containing mercury. The purpose of using the second beaker is to trap any mercury carried over with the flowing water. The rinsing operation will last for twenty four hours to insure complete removal of contaminant and any excess acid. The water is decanted from the beaker and the mercury is poured into a funnel with filter paper that has a pin hole at the bottom. The filter paper absorbs water leaving the mercury in dry condition. This filtering process was repeated two to three times. The shiny dry mercury is then ready for reuse in the next calorimeter experiment.

6.2.5 Flotation Experiments

The coal samples of varying particle sizes were used in the flotation experiments. They were 48 x 100 mesh, 100 x 200 mesh, 200 x 325 mesh and <400 mesh respectively and the weight of each sample used was 200 g. The sample was first placed in the flotation
Figure 8. Calibration Curve for Calorimetry
Experimental Value = 4223.4 cal/mol
Literature Value = 4199.8 cal/mol

Figure 9. Potassium Chloride Calibration Curve
cell of Denver laboratory flotation machine and agitated in water for about 30 minutes. The operation is necessary to ensure the complete wetting of the coal surfaces. The slurry was diluted to 4,000 ml with the addition of deionised water to produce a 5% solid concentration. The MIBC (i.e., Methyl Isobutyl Carbinol) concentration of 0.5 lb/ton of coal and kerosene concentration of 3.0 lb/ton of coal were added to the slurry and the cell was left for about 30 seconds conditioning time before initiating the flotation experiment. The speed used in all flotation experiments was 1300 rpm. The air was introduced into the cell by opening a release valve and the slurry was left agitated for at two minutes before collecting the concentrate. Both concentrate and tailings were filtered, dried and weighed at the end of each experiment to evaluate the percent recovery of coal. Three experimental runs were conducted for each coal particle size and the values of percent recovery were noted.
7.0 RESULTS AND DISCUSSION

The objective of utilizing the Setaram C-80 heat-flux microcalorimeter in this research work is to perform the heat of immersion of coal in various liquids. The results are then used to characterize the solid in terms of hydrophobicity/hydrophilicity. Flotation experiments were also conducted on the coal samples of different particle sizes.

7.1 Calorimeter Operation

The calibration procedure of the instrument was done by measuring the heat of dissolution of potassium chloride at 301 K. The purpose of calibration is to verify the optimum performance of the instrument. The results of the calibration were compared with the literature value and agreed reasonably well, within 1.20%. The procedure was repeated once every month to ensure the proper operation of the calorimeter. The calibration curve using potassium chloride is shown in Figure 9 resulting in a heat of dissolution value of 4223.4 cal/mol (0.56% error).

Pittsburgh seam coal was used in these experiments, utilizing different particle sizes of 30 x 50 mesh (0.295 - 0.589 mm), 50 x 100 mesh (0.147 -0.295 mm), 100 x 200 mesh (0.074 - 0.147 mm), 200 x 325 mesh (0.043 - 0.074 mm), and ≤400 US mesh ( <0.038 mm) respectively. The heat of immersion study was conducted using water, 20% methanol-water, and a mixture of flotation agents (i.e.,
mixture of 1 L water with 90 µl of kerosene and 15 µl of MIBC). The work was done in the isothermal mode of operation, at a temperature of 303 K. The experiment was performed three times for each particle size of one type of immersional liquid to verify the reproducibility of the results. Reproducibility of the experimental data was very good for all sizes of coal samples. The $\Delta H_{imm}$ was determined to be $-0.5636 \pm 0.0127$ cal/g in water, $-0.9841 \pm 0.0065$ cal/g in 20% methanol-water, and $-0.0947 \pm 0.0017$ cal/g in the mixture of flotation agents for particle size 30 x 50 mesh (0.295 - 0.589 mm).

7.2 Effect of Particle Size

In all of immersional liquids used in this study, the $\Delta H_{imm}$ (on a unit weight basis) values were found to increase with decreasing particle size of coal sample. The explanation to the increasing values in $\Delta H_{imm}$ was provided in terms of increasing structural disorder of the coal material. As the particle size decreased sufficiently, the core material diminished and the resultant material flexed much more freely to accept the wetting medium. He further emphasized that other factors such as mineral content, coal rank, thermal modifications, etc., had to be included in studying the behavior of increasing $\Delta H_{imm}$ with particle size. Chawla and Arnett(44), on the other hand, did not observed the change in $\Delta H_{imm}$ with particle size of 80 x 400 mesh, 45 x 60 mesh, and 230 x 375 mesh.
The average particle sizes of the Pittsburgh seam coal used in this investigation were measured by a Leeds and Northrup Microtrac particle-Size Analyzer. The results of the analysis revealed the average particle size of 0.4149 mm, 0.2173 mm, 0.1107 mm, 0.0551 mm, and 0.0215 mm for 30 x 50 mesh, 50 x 100 mesh, 100 x 200 mesh, 200 x 325 mesh, and <400 US mesh sample respectively. The comparison of particle size with the surface area given in Table A-5 shows that as coal particle size decreases the available surface area increases. The surface area measurements were done using four different techniques. The first method involved in measuring the average particle diameters assuming that the coal particle was made up of spherical particles. The external surface area was then calculated. The second technique of measuring the external surface area was conducted at Pittsburgh Energy Technology Center (PETC) with the aid of a reflected light microscope interfaced with an IBAS image analyzer. The coal samples were first prepared in one-inch diameter pellets for each particle size. Their surfaces were carefully polished. The perimeter as well as the cross-sectional area were measured and detected in randomly selected fields across the surface of the pellet. In order to ensure that no incorrect particles were sized, an editing step was adopted to separate touching particles and to fill in some areas that would otherwise have been misread by IBAS. The ratio of the perimeter to cross sectional area measurement was proportional to the surface area to volume ratio\(^6\). These values were then used with the coal density to evaluate the measured external surface area on a unit weight
basis.

The third method was done at the University of Pittsburgh Applied Research Center using low temperature krypton adsorption BET surface areas. Initially, the coal samples were outgassed for four continuous hours at 200°C with nitrogen gas. This was then followed by the BET surface area measurements using krypton at 77 K. The use of krypton in the BET method was highly recommended for low surface area powders. The last technique of surface area determination was performed at the University of Pittsburgh’s Chemical and Petroleum Engineering Department using carbon dioxide gas. The coals samples were first outgassed overnight which was later followed by the CO₂ BET surface area determination at 393 K. The use of carbon dioxide had been known to be the most promising sorption system to measure completely the surface area of microfine structure of coal\(^{(28,29,61)}\), based on the carbon dioxide adsorption BET surface analysis. The work was completed at the University of Pittsburgh’s Chemical and Petroleum Engineering Department. The values of surface area obtained by all four techniques were tabulated in Table B-5.

It is generally known that hydrophilic solids are characterized by higher values of heat of immersion in organic liquids than in water. In this research experiments, methanol is used as organic immersional liquid to characterize a solid in terms of hydrophobicity or hydrophilicity. Pittsburgh seam coal is a relatively hydrophobic coal, so by using the 20% methanol-water mixture the complete wetting of the coal surface will be ensured.
The values of $\Delta H_{\text{imm}}$ are plotted versus particle sizes in all three different immersional liquids (i.e., water, 20% methanol-water, and a mixture of flotation agents) and are presented in Figures 10, 11, 12, and 13. The heat of immersion was evaluated on a unit weight basis and was noted to increase with decreasing particle size in all cases. The graph of measured external surface area versus heat of immersion is also plotted in Figure 14 and 15. The expected behavior of increasing $\Delta H_{\text{imm}}$ with increasing surface area is observed which indicating that the more area available on the surface of coal the higher the heat of immersion would be.

The high degree of hydrophobicity of bituminous HVA Pittsburgh seam coal will prevent complete wetting by water. The use of methanol in the immersional liquid, on the other hand, is suitable for the purpose of achieving more effective wetting on the coal surface as well as smaller particle size ranges to be used in the heat of immersion experiments.

7.3 Heat of Immersion with other Liquids

7.3.1 Methanol

Several research workers\(^6\text{-}^9\) have in the past measured the heat of immersion with the objective of identifying solids in terms of hydrophobicity and hydrophilicity. The understanding from such extensive studies is that higher heat of immersion is expected by hydrophobic solids in organic liquids than in water. The reverse is true for the case of hydrophilic solids. The predominantly
hydrophobic characteristic of coal was confirmed by Melkus et al.\(^9\) who conducted heat of immersion measurements in methanol on MV bituminous Upper Freeport seam, Pittsburgh seam, Illinois No. 6 seam coal, Mammoth seam coal, Rosebud seam coal, Graphite, Pyrite, Slate, and Beulah Zap seam coal. They observed the highest \(\Delta H_{\text{imm}}\) values on Beulah Zap seam coal indicating the most hydrophobic solid, followed by Rosebud seam coal and Illinois No.6 seam coal.

The measurements on the heat of immersion were made in 20% methanol-water mixture and the results were compared to the measurements done with water as immersionsal liquid. The complete experimental data were tabulated in Table A-6, A-7, and A-8.

The values of \(\Delta H_{\text{imm}}\) of all coal particle sizes are higher in 20% methanol-water mixture than in water. This is to be expected since 20% methanol-water is capable of wetting the coal surface completely as well as more polarity. The same phenomena was also noted by Glanville et al.\(^{22}\) who investigated the heat of immersion studies using more hydrophobic Pocahontas No. 3 seam coal and Pocahontas No. 3 seam coal dust. The two types of coal were thoroughly wetted by 20% methanol-water. The methanol was chosen as the immersionsal liquid due to its ability to penetrate effectively the coal structure. Widyani et al.\(^{20}\) noted that the alcohol chain length of the immersionsal liquid increases non-linearly with decreasing heat of immersion. They concluded that such phenomena was related to the limited accessibility of longer chain n-alcohol to the coal structure.
Figure 10. Effect of Particle Size on Heat of Immersion in Water (30-35 mg of sample in 5 ml of water)
Figure 11. Effect of Particle Size on Heat of Immersion in 20% Methanol–Water (30–35 mg of sample in 5 ml of water)
Figure 12. Effect of Particle Size on Heat of Immersion in a Mixture of Flotation Agents (30–35 mg of sample in 5 ml of water)
Heat of Immersion (cal/g)

Average Particle Size (mm)

Figure 13. Effect of Particle Size of Bituminous HVA Pittsburgh Seam Coal on Heat of Immersion
Figure 14. Measured External Surface Area versus Heat of Immersion in all Immersional Liquids
Figure 15. Total Surface Area versus Heat of Immersion in all Immersional Liquids
7.3 Flotation Agents

The two types of flotation agents used in this research work were MIBC frother and kerosene collector. They are known and used extensively in the flotation experiments to facilitate the production of stable froths by changing the surface tension of the water. The molecular structure is characterized by one polar constituent at one end and nonpolar at the other. The use of collector in the flotation experiments is to encourage better contact between the coal particles and air bubbles by forming a thin coating over the particle to be floated rendering the particle water-repellent.

Melkus et al. (9) have studied the effect of varying the concentration of kerosene and pH of the emulsion on the values of $\Delta H_{imm}$ of Illinois No. 6 seam coal. The kerosene concentrations used were 0, 18, 90, and 163 $\mu l/l$ of water while MIBC concentration was held constant at 15 $\mu l/l$ of water throughout the entire investigation. They observed that $\Delta H_{imm}$ values were decreasing with increasing concentration of kerosene indicating a slightly more hydrophobic solid. The use of kerosene in the flotation is known to increase the recovery by means of adsorption onto the surface of particles. This consequently will make the particles more hydrophobic. The heat of adsorption of kerosene which is of the same order of magnitude to that of heat of immersion occurs on specific sites on the coal surface. The higher concentration of bulky kerosene molecule means that more sites on coal surface are blocked from the water molecules thereby resulting in a decrease in
the heat of immersion, which is typical characteristic of a more hydrophobic solid. In the study of varying pH, kerosene concentration of 90 μl/l and MIBC of 15 μl/l of water were tried. The pH was adjusted accordingly by the addition of sulfuric acid or sodium hydroxide. They noted the minimum value of $\Delta H_{\text{imm}}$ occurred at pH between 6.5 and 7.0 and found that the highest flotation recovery was achieved within that pH range.

The flotation process on Pittsburgh seam coal of varying particle sizes was carried out with 15 μl/l MIBC concentration (i.e., 0.5 lb/ton of coal) and kerosene of 90 μl/l of water concentration. The increase in the flotation recovery was observed as the particle size increases as shown in Figure 16. This behavior is attributed to the more ability of the flotation agents to penetrate the pore structure of larger particle size coal. The decrease in the heat of immersion on the smaller particle size might be due to the difficulty in penetrating the coal structure as a result of possible surface oxidation taking place on the surface.
Figure 16. Effect of Particle Size on the Heat of Immersion and Flotation Recovery of Pittsburgh Seam Coal
8.0 CONCLUSIONS

The heat of immersion values are critical in the study of characterization of solid in terms of hydrophobicity or hydrophilicity. They are equally valuable in better understanding of surface properties of solid. The main objective of this research work is to confirm the existence of correlation between the heat of immersion and particle size in various immersional liquids. The conclusions that can be drawn from the investigation are presented below:

1. The heat of immersion of Pittsburgh seam coal in water, in unit weight basis, was found to increase with decreasing particle size. This could be explained in terms of more available surface area on the coal surface to be exposed to the wetting liquid.

2. When 20% methanol-water was used as immersional liquid instead of just water, approximately a two-fold increase in $\Delta H_{imm}$ was noted indicating more polarity of the liquid which results in more complete wetting of hydrophobic Pittsburgh seam coal. The interpretation of such behavior in the kinetic of immersion can be provided in terms of high degree of penetration of methanol into the pore structure.

3. A similar trend of increasing heat of immersion with decreasing particle size was also observed in 20% methanol-water. Again, as the particle size decreases the more
surface area will be available for contact with immersional liquid.

4. The heat of immersion values were found to be the smallest when flotation agents were incorporated in the study. This is expected since the bulky molecule of kerosene has great tendency to block the sites of the coal surface from water which in turn results in the decrease of heat of immersion.

5. The increase in $\Delta H_{imm}$ as particle size decreases was also seen when flotation agents were used. The cause of such increase is related to the availability of more surface area on the coal surface as explained earlier.

6. The conclusion that can be drawn from this investigation is that heat of immersion of bituminous HVA Pittsburgh seam coal is indeed correlated exponentially with particle size in various immersional liquids. The correlation can be represented by the following equations:

   (a). In Water:
   $$ Y = \exp(-1.90X) \times 1.25 $$

   (b). In 20% Methanol-Water:
   $$ Y = \exp(-2.34X) \times 2.62 $$

   (c). In Flotation Agent:
   $$ Y = \exp(-4.24X) \times 0.52 $$

where $Y$ - heat of immersion on a calorie per gram basis

   $X$ - average particle size in millimeter
9.0 RECOMMENDATIONS

One of the difficulties in running the instrument is the sensitivity of the unit to temperature change in the laboratory where the measurement is conducted. Similar experiment can be performed at several elevated temperatures which may hopefully diminish the interference effect of such changes in temperature to the small heat of immersion values. This research work can also be used in studying the effect of temperature on $\Delta H_{\text{imm}}$.

The use of transparent plastic to cover the instrument would ideally help in reducing the fluctuation in temperature. The introduction of computerized integrator could be incorporated with the instrument that would minimize the error in the integration of the calibration curve of heat of immersion.
### TABLE A

**APPENDIX A**

<table>
<thead>
<tr>
<th>Class</th>
<th>Value</th>
<th>Value Type</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
<th>Value 4</th>
<th>Value 5</th>
<th>Value 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>2.</td>
<td>3.</td>
<td>4.</td>
<td>5.</td>
<td>6.</td>
<td>7.</td>
<td>8.</td>
<td>9.</td>
</tr>
</tbody>
</table>

Note: Table values are approximate and subject to revision based on further analysis.

2. Definitions and methods of calculations are subject to revision.

3. Additional information and data points are subject to further investigation.
Table A-1. Classification of Coals by Rank

<table>
<thead>
<tr>
<th>Class</th>
<th>Group</th>
<th>Fixed Carbon Limits, percent (Dry, Mineral-Matter-Free Basis)</th>
<th>Volatile Matter Limits, percent (Dry, Mineral-Matter-Free Basis)</th>
<th>Calorific Value Limits, Btu per pound (Moist(^1) Mineral-Matter-Free Basis)</th>
<th>Agglomerating Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Anthracite</td>
<td>1. Meta-anthracite</td>
<td>98 Greater Than 98 Less Than</td>
<td>2 Greater Than 2 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Nonagglomerating^2</td>
</tr>
<tr>
<td>I. Anthracite</td>
<td>2. Anthracite</td>
<td>92 Greater Than 92 Less Than</td>
<td>8 Greater Than 8 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>I. Anthracite</td>
<td>3. Semianthracite</td>
<td>86 Greater Than 92 Less Than</td>
<td>6 Greater Than 6 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>II. Bituminous</td>
<td>1. Low volatile bituminous coal</td>
<td>78 Greater Than 86 Less Than</td>
<td>14 Greater Than 14 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>II. Bituminous</td>
<td>2. Medium volatile bituminous coal</td>
<td>69 Greater Than 78 Less Than</td>
<td>22 Greater Than 22 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>II. Bituminous</td>
<td>3. High volatile A bituminous coal</td>
<td>69 Greater Than 69 Less Than</td>
<td>31 Greater Than 31 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>II. Bituminous</td>
<td>4. High volatile B bituminous coal</td>
<td>78 Greater Than 78 Less Than</td>
<td>22 Greater Than 22 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>II. Bituminous</td>
<td>5. High volatile C bituminous coal</td>
<td>78 Greater Than 78 Less Than</td>
<td>22 Greater Than 22 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>III. Subbituminous</td>
<td>1. Subbituminous A coal</td>
<td>78 Greater Than 78 Less Than</td>
<td>14 Greater Than 14 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>III. Subbituminous</td>
<td>2. Subbituminous B coal</td>
<td>78 Greater Than 78 Less Than</td>
<td>14 Greater Than 14 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>III. Subbituminous</td>
<td>3. Subbituminous C coal</td>
<td>78 Greater Than 78 Less Than</td>
<td>14 Greater Than 14 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Commonly Agglomerating</td>
</tr>
<tr>
<td>IV. Lignite</td>
<td>1. Lignite A</td>
<td>98 Greater Than 98 Less Than</td>
<td>14 Greater Than 14 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Nonagglomerating^2</td>
</tr>
<tr>
<td>IV. Lignite</td>
<td>2. Lignite B</td>
<td>98 Greater Than 98 Less Than</td>
<td>14 Greater Than 14 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Nonagglomerating^2</td>
</tr>
<tr>
<td>IV. Lignite</td>
<td>3. Lignite C</td>
<td>98 Greater Than 98 Less Than</td>
<td>14 Greater Than 14 Less Than</td>
<td>Equal or Greater Than 14 Less Than 14</td>
<td>Nonagglomerating^2</td>
</tr>
</tbody>
</table>

^1 Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

^2 If agglomerating, classify in low-volatile group of the bituminous class.

^3 Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.
Table A-2. Approximate Values of Some Coal Properties in Different Rank Ranges

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>X C (min. matter free)</td>
<td>65-72</td>
<td>72-76</td>
<td>76-78</td>
<td>78-80</td>
<td>80-87</td>
</tr>
<tr>
<td>X H</td>
<td>4.5</td>
<td>3</td>
<td>5.5</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>X O</td>
<td>30</td>
<td>18</td>
<td>13</td>
<td>10</td>
<td>10-4</td>
</tr>
<tr>
<td>X O as COOH</td>
<td>13-10</td>
<td>5-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>X O as CH</td>
<td>15-10</td>
<td>12-10</td>
<td>9</td>
<td>?</td>
<td>?</td>
</tr>
<tr>
<td>Aromatic C atoms x of total C</td>
<td>50</td>
<td>65</td>
<td>?</td>
<td>?</td>
<td>75</td>
</tr>
<tr>
<td>Av. no. benz. rings/layer</td>
<td>1-2</td>
<td>1</td>
<td>2-3</td>
<td></td>
<td>37</td>
</tr>
<tr>
<td>Volatile matter, X</td>
<td>40-50</td>
<td>35-50</td>
<td>35-45</td>
<td>?</td>
<td>31-40</td>
</tr>
<tr>
<td>Reflectance, X, vitrinite</td>
<td>0.2-0.3</td>
<td>0.3-0.4</td>
<td>0.5</td>
<td>0.6</td>
<td>0.6-1.0</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>increases</td>
</tr>
<tr>
<td>Total surface area</td>
<td></td>
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<td></td>
<td></td>
<td>minimum</td>
</tr>
<tr>
<td>Plasticity and coke formation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>only</td>
</tr>
<tr>
<td>Calorific value, moist.</td>
<td>7,000</td>
<td>10,000</td>
<td>12,000</td>
<td>13,500</td>
<td>14,500</td>
</tr>
<tr>
<td>Min. matter free, Btu/lb.</td>
<td></td>
<td></td>
<td></td>
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Table A-3. Ultimate and Proximate analysis of Bituminous HVA Pittsburgh Seam Coal

<table>
<thead>
<tr>
<th></th>
<th>PROXIMATE ANALYSIS (AS RECD)</th>
<th>(MOIST FREE)</th>
<th>(MOIST &amp; ASH FREE)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Moisture</strong></td>
<td>1.93</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Volatile Matter</strong></td>
<td>37.93</td>
<td>38.68</td>
<td>40.85</td>
</tr>
<tr>
<td><strong>Fixed Carbon</strong></td>
<td>54.92</td>
<td>56.00</td>
<td>59.15</td>
</tr>
<tr>
<td><strong>Ash</strong></td>
<td>5.22</td>
<td>5.32</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**ULTIMATE ANALYSIS**

<table>
<thead>
<tr>
<th></th>
<th>(AS RECD)</th>
<th>(MOIST FREE)</th>
<th>(MOIST &amp; ASH FREE)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Hydrogen</strong></td>
<td>4.92</td>
<td>4.80</td>
<td>5.07</td>
</tr>
<tr>
<td><strong>Carbon</strong></td>
<td>83.34</td>
<td>84.98</td>
<td>89.76</td>
</tr>
<tr>
<td><strong>Nitrogen</strong></td>
<td>1.45</td>
<td>1.48</td>
<td>1.57</td>
</tr>
<tr>
<td><strong>Sulfur</strong></td>
<td>1.12</td>
<td>1.14</td>
<td>1.21</td>
</tr>
<tr>
<td><strong>Oxygen (IND)</strong></td>
<td>3.94</td>
<td>2.27</td>
<td>2.40</td>
</tr>
<tr>
<td><strong>Ash</strong></td>
<td>5.22</td>
<td>5.32</td>
<td>N/A</td>
</tr>
</tbody>
</table>

**HEATING VALUE (BTU/LB)**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>14241</strong></td>
<td>14347</td>
<td>14946</td>
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</tbody>
</table>

**SULFUR FORMS**

<table>
<thead>
<tr>
<th></th>
<th>(AS RECD)</th>
<th>(MOIST FREE)</th>
<th>(MOIST &amp; ASH FREE)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sulfate</strong></td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td><strong>Pyritic</strong></td>
<td>0.56</td>
<td>0.56</td>
<td>0.59</td>
</tr>
<tr>
<td><strong>Organic</strong></td>
<td>0.48</td>
<td>0.48</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**MAJOR ELEMENTS IN ASH**

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>56.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>25.39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>9.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>1.23</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table A-4. Dry Screen Analysis of Bituminous Pittsburgh Seam Coal

<table>
<thead>
<tr>
<th>Screen Size (US Mesh)</th>
<th>Bottom Size</th>
<th>Openings, µm</th>
<th>Weight (g)</th>
<th>Percent</th>
<th>Cumm %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt; 30</td>
<td>590</td>
<td>33.1</td>
<td>6.22</td>
<td>99.9</td>
</tr>
<tr>
<td></td>
<td>30 x 50</td>
<td>419</td>
<td>176.4</td>
<td>33.1</td>
<td>93.7</td>
</tr>
<tr>
<td></td>
<td>50 x 100</td>
<td>210</td>
<td>144.4</td>
<td>27.1</td>
<td>60.6</td>
</tr>
<tr>
<td></td>
<td>100 x 200</td>
<td>105</td>
<td>91.1</td>
<td>17.1</td>
<td>33.5</td>
</tr>
<tr>
<td></td>
<td>200 x 325</td>
<td>57</td>
<td>55.1</td>
<td>10.4</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>325 x 400</td>
<td>40</td>
<td>24.1</td>
<td>4.53</td>
<td>6.00</td>
</tr>
<tr>
<td></td>
<td>&lt; 400</td>
<td>37</td>
<td>7.80</td>
<td>1.47</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td>Total=</td>
<td></td>
<td></td>
<td></td>
<td>99.9</td>
</tr>
</tbody>
</table>

Total: 532.0
Table A-5. Surface Area of Bituminous HVA Pittsburgh Seam Coal

<table>
<thead>
<tr>
<th>Particle Size Range (US Mesh)</th>
<th>Calculated External</th>
<th>Measured External</th>
<th>Krypton Adsorption</th>
<th>CO₂ Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 x 50</td>
<td>0.0103</td>
<td>0.0130</td>
<td>0.1989</td>
<td>34.0</td>
</tr>
<tr>
<td>50 x 100</td>
<td>0.0197</td>
<td>0.0258</td>
<td>0.2774</td>
<td>35.4</td>
</tr>
<tr>
<td>100 x 200</td>
<td>0.0387</td>
<td>0.0522</td>
<td>0.3728</td>
<td>71.4</td>
</tr>
<tr>
<td>200 x 325</td>
<td>0.0778</td>
<td>0.2370</td>
<td>1.1916</td>
<td>102.0</td>
</tr>
<tr>
<td>&lt; 400</td>
<td>0.1993</td>
<td>0.5174</td>
<td>N/A</td>
<td>122.4</td>
</tr>
</tbody>
</table>
Table A-6. Effect of Average Particle Size on the Heat of Immersion in Water

<table>
<thead>
<tr>
<th>Particle Size (mm)</th>
<th>Measured Value</th>
<th>Average Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4149</td>
<td>0.5491, 0.5725, 0.5692</td>
<td>0.5636 ± 0.0127</td>
</tr>
<tr>
<td>0.2173</td>
<td>0.8395, 0.8516, 0.8429</td>
<td>0.8447 ± 0.0062</td>
</tr>
<tr>
<td>0.1107</td>
<td>1.0400, 0.9815, 1.0044</td>
<td>1.0086 ± 0.0295</td>
</tr>
<tr>
<td>0.0551</td>
<td>1.1175, 1.1197, 1.1156</td>
<td>1.1176 ± 0.0021</td>
</tr>
<tr>
<td>0.0215</td>
<td>1.2151, 1.1921, 1.1975</td>
<td>1.2016 ± 0.0120</td>
</tr>
<tr>
<td>Particle Size (mm)</td>
<td>Measured Value</td>
<td>Average Value</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------</td>
<td>---------------------</td>
</tr>
<tr>
<td>0.4149</td>
<td>0.9916, 0.9812, 0.9796</td>
<td>0.9841 ± 0.0065</td>
</tr>
<tr>
<td>0.2173</td>
<td>1.6341, 1.5765, 1.6468</td>
<td>1.6191 ± 0.0375</td>
</tr>
<tr>
<td>0.1107</td>
<td>1.9192, 1.9455, 1.9055</td>
<td>1.9234 ± 0.0203</td>
</tr>
<tr>
<td>0.0551</td>
<td>2.3990, 2.3027, 2.3928</td>
<td>2.3648 ± 0.0539</td>
</tr>
<tr>
<td>0.0215</td>
<td>2.4779, 2.4844, 2.4752</td>
<td>2.4792 ± 0.0047</td>
</tr>
</tbody>
</table>

Table A-7. Effect of Average Particle Size on the Heat of Immersion in 20% Methanol-Water
Table A-8. Effect of Average Particle Size on the Heat of Immersion in a Mixture of Flotation Agents (i.e., 15 μl of MIBC and 90 μl of Kerosene in 1 L of Water)

<table>
<thead>
<tr>
<th>Particle Size (mm)</th>
<th>Measured Value</th>
<th>Average Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4149</td>
<td>0.0960, 0.0953, 0.0928</td>
<td>0.0947 ± 0.0017</td>
</tr>
<tr>
<td>0.2173</td>
<td>0.1889, 0.1906, 0.1878</td>
<td>0.1891 ± 0.0014</td>
</tr>
<tr>
<td>0.1107</td>
<td>0.3288, 0.3263, 0.3311</td>
<td>0.3287 ± 0.0024</td>
</tr>
<tr>
<td>0.0551</td>
<td>0.4243, 0.4258, 0.4226</td>
<td>0.4242 ± 0.0016</td>
</tr>
<tr>
<td>0.0215</td>
<td>0.4937, 0.4920, 0.4906</td>
<td>0.4921 ± 0.0016</td>
</tr>
</tbody>
</table>
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