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Dewatering of fine coal slurries by selective heating with microwaves

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DEWATERING OF FINE COAL SLURRIES BY SELECTIVE HEATING WITH MICROWAVES

**By
AASHISH KALRA**

Thesis

**Submitted to the College of
Engineering and Mineral Resources
At
West Virginia University**

**In Partial Fulfillment of the Requirements
For the Degree of
Master of Science in Mechanical Engineering**

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Coal, Drying.**

ABSTRACT

DEWATERING OF FINE COAL SLURRIES BY SELECTIVE HEATING WITH MICROWAVES

Since water is used extensively in coal preparation and cleaning, dewatering of coals is required prior to shipment to power plants. However, finer fractions of coals are difficult to dewater and consequently these fractions are stored in settling ponds, causing environmental problems and loss of a large fraction of coals. Thermal drying of coals is not an efficient process since hot air heats both coal and water. Mechanical processes for dewatering fine coal slurries have a limit for dewatering coal. Consequently, dewatering using selective heating by conventional microwaves at 2.45 GHz and IR heating at 10^{14} Hz was undertaken as the primary focus of this project. The basis for this choice is the fact that theoretically water absorbs 120 times more microwave energy than coal. TGA and DSC were initially employed to determine the process of dewatering by thermal heating. Then using gram quantities of fine coal slurries, a conventional microwave oven was used to determine the efficiency of dewatering by selective microwave heating. X-ray diffraction of the 'before' and 'after' microwave treated coal slurry showed that the coal carbon is not affected by microwave treatment. Finally, a conventional microwave oven was modified to feed coal on a conveyor-belt to simulate a potential commercial unit.

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DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, nor assume any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or agency thereof.

DEDICATION

I dedicate this work with lots of love and affection to my parents- Dr. (Mrs.) Nirmal Kalra and Dr. Ramesh Chandar Kalra, as I would never have come this far without their infinite encouragement and guidance through all phases of my life. Also I would like to dedicate this work to my sister, brother-in-law and their newly born daughter Shria.

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1. INTRODUCTION

Coal is complex yet abundantly available energy source. According to a survey coal provides around 26% of global primary energy needs and generates about 37% of world's electricity (Press release, 2005). It has been estimated that there are around one thousand billion ton of coal reserves economically accessible using current mining technology and the current coal reserves/production ratio confirm 200 years of resources available. Thus coal will remain to be a dominant energy source. The US has the largest coal reserves in the world. Apart from being used as an energy source for generating electricity, coal is also used in various other industries and manufacturing plants for the production of coke, cement, paper, syngas, and chemicals and also as a house hold fuel. Research is on for using coal for applications in alternative fuel (Williams & George, 1988; Nielsen, Bodil, Bogild and Schiodt, 2005; Grethlein & Jain, 1992).

The use of coal for any application creates several problems as it is a highly heterogeneous material and thus requires preparation and cleaning before utilization. Water is extensively used in coal preparation and cleaning. It is added into coal during grinding of coal for dust control, as well as during flotation process for removing undesirable minerals from coal. The composition of coal varies from site to site and even at different levels of mining due to which coal cleaning is highly site specific. Due to the high efficiency of the wet cleaning methods, dry cleaning methods are rarely used in the present plants (National Research Council, 2002). The power plants are engineered for optimal combustion to burn coal with specific mineral, moisture and heat content. Thus coal once prepared and cleaned, contains large amounts of moisture and this moisture should be removed for practical usage of coal.

Various techniques are used for dewatering coal such as filtration, vacuum drying, centrifugation and thermal drying. However it is important to know that only the free water in coals can be easily removed by mechanical techniques. Coal structure is highly porous and thus the interaction of water with coal is very complicated. Thus a large quantity of water in coal is “bound water” which is attached to the coal structure by hydrogen bonds and as water of hydration. With the improvements in mining technology, higher quantities of finer coal fractions are obtained, and due to the large surface area of the mined coal, it is very difficult to dewater it. Thus mechanical drying methods are deemed well only for larger fractions and also has a limit of dewatering achieved (Dzinomwa, 1997).

Thermal (conventional) dewatering is widely used for dewatering coal but it is not economical as it heats both coal and water (Ranjan & Hogg, 1996). It also causes irreversible changes in coal which results in the loss of BTU and added pollution (Beuerman, 1986). There are other problems associated with thermal (conventional) heating such as considerable fugitive air, potentially explosive mixtures developed in stack and environmental problems in connection with disposal and settling ponds. Thermal drying is slow and the rate is limited by the rate of conductivity as only the surface is heated. In this kind of drying there is an internal resistance to the heat flow due to low thermal conductivity and the large overall dimension of the wet coal. This causes the surface temperature to reach that of the adjacent air stream thus reducing the heat flow to the solid and creating significant temperature gradient. In the absence of an effective and efficient dewatering process for fine coal fractions, large amounts of fine coals are relegated to nearby ponds. These ponds are not only waste of valuable energy

and land but also pose as environmental threat. Due to the inefficiencies in dewatering and cleaning processes, out of 400-500 million tons of coal washed in U.S. each year less than half the finer coal fractions are cleaned and thus increasing the problems of settling ponds. The coal slurry impoundments are classified usually as active, inactive and abandoned. In the U.S. alone, around 2 billion tons of fine coal is lying in as many as 713 active ponds (according to 2001 data), especially in states of West Virginia, Virginia and Kentucky (Vendetti, 2001).

Thus search for new techniques for dewatering of coal is a subject long studied for improving the present dewatering techniques and to utilize large amounts of coal present in the waste ponds. During the present energy crisis, interest is being shown in the coal relegated to ponds (Mahamud, Corte & Sastre, 2002). These coal slurries are a mixture of water, fine coal, sand, silt and clay particles. Proper identification and quantification of different impurities is important for developing efficient cleaning methods. New techniques for cleaning these fine coals from the ponds are being developed for making the slurry coal industrially viable (News Release, DTE Energy, 2003). Various different dewatering techniques have been studied in the past years (Gehreke, Lyu & Barnthouse, 1998; Gerl & Stahl, 1996; Dzinomwa, Wood & Hill, 1997; Bourgeois & Haque, 2000), but still the industry is looking for an economical, efficient and easy way to dewater coal. In this study we have looked at the effectiveness of microwave and infrared irradiation to dewater coal. The basis for this choice is the fact that water absorbs more energy in the microwave and infrared frequencies than coal. (Lindroth, 1985; Babu, Farinash & Seehra, 1995). Using different coal samples, experiments were first done on gram quantities of samples with TGA

(Thermogravimetric analysis), DSC (Differential Scanning Calorimetry) and XRD (X-ray diffraction) to understand the dewatering process and the effect of microwave heating on water, coal carbon and ash in coal slurries. The microwave source for all our work was a conventional, store-bought microwave oven (800 Watts). For the IR experiments, a commercial electric IR heater was used with a watt density of 25Watt/inch². The microwave experiments showed that dewatering by microwave heating is indeed an efficient process approaching near 80% of the maximum theoretical efficiency. So a laboratory scale microwave dewatering unit with a conveyor-belt feed system was designed to simulate a potential commercial unit, with appropriate microwave shielding and remote control operation. In this unit, 83% efficiency (relative to the maximum theoretical limit) for dewatering of fine coal slurry was obtained. Our cost estimate to remove 10% moisture from coal slurry at 0.04\$/kWh using microwave heating is about \$3/ton of the slurry. XRD spectroscopy was also used to identify and quantify different inorganic phases in the coal. A theoretical method was developed to find the percentage content of Kaolinite and Illite in different coal using XRD spectra and information from Atomic absorption. These results were compared with the results obtained using a commercial Rietveld software. These two methods gave quite close results and thus giving confidence to the theoretical method.

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2. BACKGROUND

2.1 Overview

This chapter gives the background on coal water interactions, various processes involved in the coal beneficiation, coal science and the use of advance techniques and instruments in coal science. Also included are the various novel techniques developed to dewater coal and the theoretical aspects of the use of microwave to dewater coal.

2.2 General Aspects- Origin of water in coal

Coal is very complex in the nature of its formation and the variety and diversity of impurity it contains. Water is inherent in coal and has a significant role in formation and utilization of coal. Coal is the end product of a sequence of biological and geological processes (Moyers et al). Movable coal seams derive from expansive peat deposits of the past. For peat to accumulate requires a moist environment such as a peat swamp to persist long enough so that plants and parts of plant that have dried can be sealed from degradation in quantity. Various mineral matters get added to the coal during this process. Once incorporated in the peat, the plant material itself undergoes rather drastic physical and chemical changes through the attack microbes within the peat bog and through increasing temperatures and pressure. Various other microorganisms and fungi attack the plant remains and break various chemical components of plants (cellulose, lignin, starch etc.) down into new components as humic acids. Humification and later gelification of woody and bark tissue in particular produce a gel like substance with the properties of a colloid which through gardening becomes vitrinite, the most common and valuable

material in coal. (Haenel, 1992) Waxes resins and natural charcoal are quite resistant to degradation and are present in higher rank coals.

As burial increases, the driving forces for the change from peat → lignite → sub bituminous → bituminous → and anthracite coal increases causing overburden pressure and higher temperature. During this process moisture is squeezed out of peat, which contains 80-90% moisture, as it is being transferred into lignite with as little as 40% moisture, sub bituminous with 20% and bituminous with 1-2% moisture.

The moisture in coal has a big effect on its measured heat capacity, which determines the cost of coal (Macdonald, 1985). The lower ranks of coal contain high amounts of moisture and needs to be dewatered. Also coal is composed of essentially every element in the periodic table. The following minerals frequently occur in coals- clay (Illite, Smectite, Kaolinite), Sulphides (Pyrites, Marcasite, Pyrrohotite), Carbonates (calcite, Dolomite), Oxides (hematite, quartz magnetite) and others such as limonite, apatite and sulphates (gypsum and barite). In order to get rid of these mineral elements from coal almost all coal requires some preparation before use. Preparation may range from simply crushing to extensive size reduction and cleaning to remove sulphur and ash forming mineral matter. Water is extensively used during these cleaning processes. Thus either due to inherent water or due to water introduced to coal during the beneficiation, all coal requires dewatering before effective utilization. In order to understand the origin of bulk water (explained in later chapter) and dewatering of coal, it is important to briefly look into various processes involved in coal beneficiation.

2.3 Processes involved in Coal Beneficiation

This section contains brief descriptions of different coal preparation plant process steps which should be understood in order to understand the dewatering process. These process are described in many standard books such as one edited by Cooper and Ellingson (1984).

As the variety and diversity of impurities in coal (form, size and relative amounts) changes both laterally and vertically, the cleaning processes applied are not the same at all sites. The mining methods also bring variations such as wet/dry or small sizes/big chunks. The surface mining and conventional underground mining methods generally produce coarse and comparatively dry solids where as continuous mining machines employed in many underground mines produce fine size solids which are wetted for dust control. But the general procedure for cleaning is to reduce size to control top size and to free or unlock occluded mineral matter followed by separation of relatively pure coal particles from particles with high mineral content. Although dry separation methods are some times used, it is more common to use wet methods or washing where in particles are separated because of differences in specific gravity between clean coal (1.3-1.7) and mineral matter (2-5). The coal is crushed and separated into coarse (+9.5mm), fine (9.5x0.6mm), and ultra-fine (-0.6mm) sizes. These separations can be done by various screens. Water sprays are applied to the screens to suppress dust. Finer sizes suspended in water are separated by vibrating screens classifying hydro-cyclones or sieve bends.

Various sizes are cleaned separately using different techniques. Generally coarse solids are cleaned by jigs or heavy media baths, fine by wet concentrating tables or heavy- media cyclones, and ultra fine particles by hydrocarbons or froth floatation. In all

these methods the solids are suspended in water, and except for froth flotation, the separation is based on the difference of specific gravity of coal and refuse particle. (Moyers et al, 1983). The various processes involved in the coal beneficiation are as follows:

2.3.1 Blending

Blending and homogenizing is used to provide the plant a uniform feed material to maximize efficiency of different processes. It is one of the most economical methods for improving the efficiency of a coal preparation plant. In addition, it is also helpful in mixing or proportioning two or more raw coals from different mine sources having different physical and chemical characteristics. By maintaining the control of blending, effectively poorer coal can be mixed in small quantities and still produce high quality coal with specific properties.

Blending schemes range from simply mixing coals from two or more raw coal stockpiles with a front-end loader to more elaborate schemes which have separate storage bins for each coal seam, with blending by automatic controls. The plant input feed rate is calculated by measuring the weight of material on the belt and multiplying by the belt speed.

2.3.2 Size Reduction

Run of mine (ROM) coal received in the coal preparation plant usually contains particles ranging in size from large lumps (>12 inch) to fines (<0.25 inch). In general, strip mining tends to produce large lumps with a small amount of fines, while continuous mining produces smaller pieces and a larger amount of fines. Most of the mines today

involve continuous mining techniques and thus the feed coal consists of higher quantities of finer coal. Various size reduction equipments such as roll crushers, rotary breakers, and hammer mills are used at the plant entrance and between processes for efficient cleaning and to meet product specification. Usually, ROM coal entering the plant is reduced to 4-6 inches top size to provide feed for the primary dense medium washers and jigs; the subsequent reduction in the coarse coal circuits is to 0.75 inch or larger. For sulfur removal it is desired to have further size reduction but finer coal sample also relate to higher moisture due to higher surface area.

2.3.3 Screens

Screening is a mechanical operation that separates particles by size by passing coal of a wide range of sizes through a series of screens, each of decreasing size. Screen size is designated in terms of Mesh Size (mesh), which is a function of the size of the opening which may be square, rectangular, hexagonal, or round. Screens, which are sometimes referred to as sieves is constructed of interwoven pore or perforated plate or rods. Wire screens are available in a wide selection of apertures from 5 inch to 500 Mesh and are used for both coarse and fine screening. Appendix I shows the conversion table for the different sieve designations (standard-mm, alternate-mesh and nominal-inch).

Coal is screened for the following reasons:

- To remove the fine coal before a size reduction step;
- To separate the coal into coarse and fine fractions for producing sized products or for cleaning in coarse and fine-coal circuits;
- To recover the dense medium from coal cleaning circuits;

- To dewater the coal product. Screening removes part of the bulk water from the large coal lumps but the water passes through the screens with the finer fractions of coal; and
- To remove rock and trash by hand picking them from the coal on a screen.

The screens used in coal preparation plant are of five types: scalpers; raw coal; pre-wet; dense medium drain and rinse; and dewatering. To increase the efficiency, most screens are mechanically actuated to circularly stroke, revolve, shake, or vibrate. Water and particles smaller than the spacing between the bars are separated from the feed by centrifugal and gravitational forces, and the resultant cake falls from the discharge at the bottom of the sieve.

2.3.4 Jigs

Jigging is a process in which a pulsating flow of fluid through a bed of particles causes the particles to stratify in layers of increasing density from the top to the bottom of the bed. Stratification of a bed is primarily due to the following effects:

- Hindered settling – free settling modified by the effects of hydraulic drag, particle collision, friction etc;
- Differential acceleration – the rate at which particles with equal settling velocities approach their terminal velocity; and
- Consolidation trickling – size-selective stratification of smaller particles by specific gravity, which occurs within a locked bed of larger particles.

Various forms of jigs are used which work on the same separation principle.

2.3.5 Dense medium cyclone

Dense medium cyclone are used for separation of fine coal having a size range typically $3/8 \times 0.02$ inch but sometimes as wide as 2×0.02 inch. The dense medium cyclone results in a sharper separation than can be obtained with other types of coal washing equipment handling the same size range. In a typical dense medium cyclone a mixture of raw coal and a dense liquid enters tangentially near the top of the cylindrical section and spirals downward. A descending vortex is formed that originates at the inlet and progresses downward to the underflow outlet. As the vortex descends, part of the liquid spins to the center of the cyclone to form an ascending vortex, which surrounds a cylindrical air core that encircles the entire longitudinal axis of the cyclone. Refuse, separated from the coal by centrifugal action, moves towards the wall of the cyclone and downward to the underflow orifice. The washed coal moves toward the longitudinal axis and passes through a vortex finder to the overflow chamber to a tangential outlet.

The dense medium is usually an unstable suspension of particles in water. The principle of operation is similar to the dense medium washer used for coarse coal separation. In both, the point of separation is determined by the effective specific gravity of the medium, and the separating action is due to the net effect of the buoyant and accelerating forces. In a typical cyclone the centrifugal force acting on a particle in the inlet region is about 20 times greater than the gravitational force in a dense medium washer. In the conical sections of coal of the cyclone, the centrifugal force increases as the inverse square of the decreasing diameter to over 200 times gravity at the apex; thus the forces tending to separate the coal and impurities are greater in the cyclone than in the

washer. Because of this the cyclone is capable of cleaning fine coals and has higher capacities.

2.3.6 Hydro-cyclones

A hydro-cyclone is similar to the dense medium cyclone, in that a centrifugal force generated by a swirling vertical flow produces a separating action, but is different in that the process fluid, in which the coal and refuse particles are suspended, is water rather than a dense medium. The separation obtained in a hydro-cyclone is not as sharp as that of a dense medium cyclone, thus hydro-cyclones are not applicable for difficult to clean coals or for separation at low specific gravities.

The major advantages of hydro-cyclone are that they are compact and require much less space than jigs or tables. The main disadvantage of hydro-cyclone is that it requires large quantities of water and high pumping power is required for proper operation.

2.3.7 Froth Flotation

Froth flotation is a physical process induced by chemicals for beneficiation of coal by segregation of a solid, valuable component (termed as a concentrate) in slurry from a less valuable material (termed as tailing) through selective attachment of bubbles to the concentrate. For effective beneficiation, the particles should be fine, less than 0.01 inch diameter. Due to increase in the use of continuous mining machines and the deliberate crushing of coal to smaller sizes to liberate impurities, the froth floatation process is being used extensively in the coal industry.

In froth floatation, chemicals are added to the coal. The groups of chemicals added can be divided into four classes:

- i. Frother, a substance which when dissolved in water and vigorously agitated with air produces stable foam. Methyl isobutyl carbinol is commonly used in the coal industry;
- ii. Collector (also called as a promoter) is added to the feed slurry to enhance the hydrophobic quality of the surface of the particles to be floated, enabling bubble attachment to the particles. Fuel oil is commonly used as in coal floatation;
- iii. Activator is added to the slurry to enhance the selective adsorption of the collector on the material to be floated;
- iv. Depressant is added to the slurry to prevent the adsorption of the collector on the gangue (worthless rock in which valuable minerals are found).

Feed slurry is obtained from the fine particle overflow of a hydro-cyclone. Reagents are added as the slurry enters the froth floatation cell. The clean coal product flows to the dewatering system and the tailings from the froth flotation cells are discharged directly to the static thickener.

2.3.8 Centrifugal Dewatering

Centrifugal dryers are usually used to dewater materials below 1.5 inch in size. The water is removed by centrifugal force created in the dryer. The most common dryers used are perforated basket machines and solid or screen bowl machines. The only control applied to a centrifugal dryer is the rotational speed required to give the optimum centrifugal force. The centrifugal drying can produce very low moisture levels for large

size coals. The surface moisture of the centrifugal product increases as the particle size becomes smaller. The centrifugal dewatering is deemed as inefficient for dewatering fine coal slurries or particles finer than 325 mesh (45 μ m standard)

2.3.9 Thermal Dryers

Thermal drying is used for dewatering finer coal particles and when a lower level of moisture is required in final product. But thermal dewatering is not deemed as cost efficient as both coal and water are heated equally. Coarser fractions of clean coal are sufficiently dewatered by screening or centrifuging. Fine coal, with large specific surface area, cannot be dewatered by mechanical means to a moisture level lower than about 15%. A vacuum filter produces a cake containing ~20% moisture, while a screen bowl centrifuge can reduce the final moisture to 12-14%. Thus for finer fractions of coal or in order to achieve lower moisture levels, thermal dewatering is used.

The thermal dryers presently used are of two types:

- Direct Heat exchangers – hot combustion gases from a furnace are forced through the coal, directly heating the coal and evaporating the moisture. These include a fluidized bed, in which the coal particles are suspended in or transported by the flowing gas stream;
- Indirect heat exchange type – hot combustion gases heat a heat transfer medium that heats and dries the coal. Steel balls, chains, steam or high temperature heat transfer liquids are used as heat-transfer medium.

2.4 Advances in Coal Science

The history of coal research dates back to year 1780 and petrology and coal chemistry developed as full grown branches of science between 1913 and 1963 (Krevelen, 1982). The coal structure and the coal water interactions are quite complex. These have attracted a lot of attention in the 20th century. A detailed study in the development and progress of coal science is described by Heek (2000). The coal structure by itself has been studied by a many researchers (Marzec, 2002; Krzesinska, 2002). Understanding the coal structure, especially the nature of attractive forces can be important in understanding the dewatering process. Effect of heat is also very important as drying coal requires heating the coal to substantially high temperatures. Thus the effect of heat on coal at different temperature ranges is an interesting topic delved by a lot of researchers (Davies & Rees, 1998; Isaccs, Abhari, Ledesema & Tsafantakis, 1992; Kolar, Radenovic & Ugarkovic, 1999).

2.4.1 Advance techniques used in Coal Science

Various advance techniques and instruments help in characterizing coal and understanding the dewatering process. The thermo-analyses (TA) studies are very important as coal undergoes heating while dewatering as well during combustion. In TA studies, properties of a sample heated at a constant rate are observed. The most common TA techniques include Thermogravimetric analysis (TGA), the Derivative Thermogravimetric (DTG) and the Differential Scanning Calorimetry (DSC) to study the thermal degradation of coal. Ozawa (1970) has discussed a method to obtain the kinetic parameters from DTG curves suitable for reactions with single activation energy.

Janikowski & Stenbert (1989) have used the thermal analysis technique (specifically TGA and DSC) to study the thermal behavior of different coal samples in the temperature range between room temperature to 600 °C. They found two regions of high chemical activity, the first being due to dewatering in the region from 75 °C- 118°C. They concluded the differential of 20°C from 100 °C in the 1st region is due to the heat transfer problems administered in coal. The DSC has been used to determine the coal specific energy. (Ma, Hill & Heng, 1991; Vargha-Butler, Soulard, Hamza & Newmann, 1982). Fourier Transformation Infra-Red (FTIR) studies have also been also used either solely or with other TA techniques to study coal water interactions. Miura, Mae & Morozumi (1997) have reported a method to determine the hydrogen bonding strength in coal water interaction by using FTIR and DSC. They concluded that the enthalpy changes are due to three processes-dissociation of water-coal hydrogen bonding, evaporation of water, and the rearrangement of hydrogen bonding in coal. Arnold (1999) developed an algorithm for predicting the moisture content of coal using various mechanical devices such as screens, centrifuges and filters. This model gives some accuracy for the free or surface moisture but concludes that inherent water in coal cannot be removed by mechanical processes and thus not incorporated by the model.

2.4.1.1 X-ray Diffraction studies

X-Ray powder diffraction (XRD) is a very important instrumental technique used to identify minerals and other crystalline materials in coal. Quantification of the mineral is important for commercial utilization of coal as these minerals may lead to problems such as boiler erosion, ash formation and slagging (Maity et al, 2003). For retrieval of coal from settlement ponds, the identification and quantification of various mineral

phases is very important as different wastes are also relegated to these ponds with finer fractions of coal. The crystal structure of non-amorphous material (crystalline) is defined by regular, repeating planes of atoms that form a crystal lattice. When a focused X-ray beam interacts with these planes, a part of it gets diffracted. The X-rays are diffracted differently by different minerals depending upon the atoms and the make up of the crystal structure. The wavelength of the X-ray depends upon the target on which the ray of electrons is hitting. The X-rays are focused on to the sample and the diffracted beam is then detected by the detector. The X-ray signal received is then processed and converted to signal to a count rate. Changing the angle between the X-ray source, the sample and the detector at a controlled rate between preset limits gives the complete scan. Then using Bragg's equation, the inter-atomic spacing or d-spacing can be calculated. The set of d-spacing generated in an X-ray scan is typical to particular mineral. The Bragg's Law is given by:

$$2 d \sin \theta = n \lambda \quad \dots\dots\dots (2.1)$$

where, n is the integer representing the order of diffracted beam, λ is the wavelength of incident X-ray beam, d is the distance between adjacent planes of atoms, and θ is the angle of incidence of the X-ray beam.

The XRD can give insight into various attributes of the cell structure. In case of mixtures of minerals, the XRD can give information such as proportion of different minerals, degree of crystallinity of the minerals and the variation from the pure composition. Apart from identification of different minerals, XRD data can also be used for quantitative analysis. Initially XRD was not highly regarded for quantitative analysis

due to effects of variations in mineral crystallinity, preferred orientation in the sample mount, and preferred absorption by some phases in the mixture (Ward, Taylor, Matulis & Dale, 2001). But presently, a lot of different methods are being used for quantification of different mineral mixtures using the XRD data. One of the methods was developed by Rietveld (Rietveld, 1969). Rietveld developed a formula to find the intensity at any angle with information to refine the crystal structure and other parameters such as background and other instrumental parameters by least square analysis of the profile. Based on the formula, using an existing XRD scan and using information about the constituents, software have been developed to generate calculated patterns to fit the observed pattern for a multi-mineral sample by iterative least square fitting. This information is used to find the percentage of individual phases. The Rietveld analysis for this work was done using MDI Jade Software with Inorganic Crystal Structure Database (ICSD) provided by NIST (ICSD, 2004). The refinements are done for the global parameters, phase parameters, global refinement and phase refinement. The global parameters are for the background and information specific to the instrument used. It takes care of background error and compensates the presence of an amorphous peak in present. The known phases are loaded in to the software. These phases consist of complete information about the d values and the Reference intensity ratios (RIR). The background iterations for this work were done for a 6th order polynomial fit and Pearson amorphous data fit when the presence of the broad carbon peak was eminent. A successful refinement is defined mathematically by the convergence of refinable parameters to meaningful values and can be gauged beside others by the ratio or difference between the two agreement factors: weighted (R) and expected (E) values. The vertical lines on the refinement screen denote

the onset of a refinement round. The R and E values are calculated by using the following formulas

$$R=100 * \text{Sqr} [\Sigma(w(i) * (I(o,i)-I(c,i))^2) / \Sigma(w(i) * (I(o,i) - I(b,i))^2)] \dots\dots\dots(2.2)$$

$$E=100 * \text{Sqr} [(N-P) / \Sigma I(o,i)] \dots\dots\dots (2.3)$$

Where, I(o,i) is the observed intensity of the fitted data point (i), I(c,i) is the calculated intensity at data point (i), I(b,i) is the background intensity at data point (i), w(i) is the statistical weight of this data point, N is the number of fitted data points, and P is the number of refined parameters.

The ratio of R/E is called the ‘goodness of fit’ and theoretically should be equal to one or in other words for a good fit the R value should be as close as possible to the E value.

2.4.2 Activation Energy

Activation energy can be used to understand the reactions occurring during the heating of coal. Activation energy (E_a) is the minimum amount of energy required for the reaction to complete. According to the Arrhenius equation

$$\log k = \log A - (E_a/2.3RT) \dots\dots\dots (2.4)$$

where, E_a is the activation energy, k is the rate constant, T is the absolute temperature, R is the gas constant (8.314 J/K-mol), and A is the frequency factor (constant).

Biswas, Kini, Das-Gupta & Lahiri (1976) have investigated the activation energies of evolution of gases in temperature range of 700°C – 800°C. Cumming (1984) has reported of a method of determining the reactivity or combustibility of solid fuels in terms of the activation energy derived from simultaneous TG (thermo-gravimetric)/DTG (Differential thermo-gravimetric) analysis. The use of activation energy to understand

the reactions occurring in plastics have been reported previously. (Ibrahim, Hopkins & Seehra, 1996; Manivannan & Seehra, 1987). Similar studies on activation energies in the temperature range of 60-140 °C can be helpful in understanding of the coal dewatering process. It is very important in understanding the details and efficiency of the dewatering process. Different techniques have been developed to measure the activation energy using TGA. (Ismail, 1992; Flynn & Wall, 1966). We have tried to use the Flynn-Wall method to calculate the activation energy of dewatering process and compare that with the expected value, which is explained in detail in the next section.

2.5 Importance of dewatering of Coal

Water is inherent in coal and is also added during grinding of coals as well as during the floatation processes used for removing unwanted minerals in mined coal. Coal needs to be dewatered for the following reasons:

1. To decrease the transportation cost;
2. To increase the heat efficiency of the burning coal by improving the heat content of coal. By reducing the amount of moisture in coal, the heat is not lost in evaporating the moisture. For burning the high moisture coal, the power plants require specially designed furnaces and boilers to ensure stable combustion and adequate heat transfer. For proper functioning of these plants, the industry has set up preset norms for the moisture and ash content;
3. To avoid difficulties during transporting the coal such as handling, freezing problems and spontaneous combustion;
4. To maintain high pulverizer capacity; and

5. To improve the quality of coal to be used for special applications such as in the productions of coke, briquettes, and chemicals.

Thus we see the origin of water in coal and the importance of dewatering the commercial coal. The coal, depending on the types, seams and particle size, may have water from 5%-60% with it. To fully understand how surface moisture can be removed from fine coal, it is necessary to understand how water is attached to coal as explained next.

2.6 Types of Water Associated With Coal

The various forms of water in coal can be defined as follows (Karr et al, 1978):

- A. Interior Adsorption Water is contained in micro pores and micro capillaries within each coal particle, deposited during formation;
- B. Surface adsorption water forms a layer of water molecules adjacent to coal molecules, but on the particle surface only;
- C. Capillary water is contained in capillaries and small crevices found in the surface of the particles;
- D. Inter-particle water is contained in capillaries and small crevices found between two or more particles;
- E. Adhesion water forms a layer or film around the surface of individual or agglomerated particles; and

The various types of water associated with coal are shown in Figure 2.1. The water that can be readily removed using mechanical fine coal dewatering devices, such as vacuum filters and centrifuges, is categorized by types D and E and is generally termed

surface moisture. Water type C can be removed partially, depending upon the size of the openings in the coal surface and the drying time available in the filter cycle. Inherent moisture is the general term used in a typical proximate analysis of coal to describe the water as defined by types A and B. These can be removed by the thermal drying processes but the conventional thermal drying is inefficient in drying the various types of water described, specially types A-D. Thus in order to evaporate water which is inside a large stack of coal, the coal is heated to a higher temperature and heat is conducted to the water trapped inside. The high temperature results in irreversible changes in coal.

Figure 2.1: Different forms of water associated with coal.

2.7 Problems with Conventional Coal Dewatering Processes

It has been established that conventional dewatering processes are inefficient and slow. For coarse coal fractions (+3/4 inch), mechanical dewatering processes such as vibrating screens and centrifugal dryers can be used to bring the moisture level to usable limits. The finer fractions of coal (<0.5mm diameter) pose greater problems in dewatering (Wilson & Ding, 1994; Yang, Wang & Parekh 1998). Due to the higher surface area, the finer fractions contain higher quantities of moisture. With the advent of new technologies in mining, higher quantities of finer coal fractions are received for cleaning, thus making dewatering more important. The mined coal is grounded to further finer sizes in order to liberate ash and sulfur minerals. Lower moisture % in coal samples can be achieved by using thermal dewatering, but use of these is minimized due to energy costs and environmental concerns (Ranjan & Hogg, 1996). There is a limit as to how much dewatering of these fine coals can be achieved by any mechanical process (Dzinomwa, Wood & Hill, 1997). Due to these reasons out of 400-500 million tons of coal washed in U.S. each year, less than half of the finer coal fractions are cleaned. These finer coal fractions are relegated to slurry disposal ponds. These ponds are not only waste of valuable carbon, they also pose severe environmental hazard. In the U.S., around 2 billion tons of fine coal is lying in as many as 713 different ponds (2001 data), especially in the states of West Virginia, Virginia and Kentucky (Vendetti, 2001). An estimated 174,000 acres of land has become waste lands in the U.S. alone. These ponds pose serious environmental problems such as degradation of water quality and the sulfides (pyrite and marcasite) get oxidized to form sulfuric acid and thus lowering the pH of local water bodies. This acidic refuse could make the wall of neighboring mining sites

weak and result in accidents and thus endangering miners. The toxic metals can also leach from refuse piles, endangering the surrounding ecosystem. Air quality also deteriorates due to the formation of airborne dust and the release of toxic gases from coal. In the past, coal impoundment failures have resulted in loss of property due to the breaking of embankment and also resulted in loss of numerous lives in Logan County, WV in an impoundment failure in 1972. Most of the mines in the United States produce a significant amount of fine size coal which could be recovered economically. Advanced processes have been developed to economically recover these fine coals but dewatering is very difficult using conventional dewatering techniques. Recently DTE PepTec has patented a new technique to commercially utilize the coal present in waste impoundments (News Release, DTE Energy, 2003).

2.8 Common minerals found with coal slurries

As explained earlier, XRD analysis can be used to identify the different impurities present in coal. The composition of coal varies a lot but a few organic phases like pyrite, quartz, illite, kaolinite and calcite are usually present in different coal in varying quantities. The details on the chemical composition of these compounds can be found in many books like Naray-szabo (1969) and is explained in this section briefly.

Pyrite (FeS_2) is a metal sulphide based on the rock salt-like packing of Fe atoms and S_2 radicals. The Fe atoms are octahedrally surrounded by six S atoms, where as sulphur atoms are surrounded by three Fe and a single S in the form of a tetrahedron. The inter-atomic distances in the S_2 radical are 2.05 Å. Other modifications are Marcasite and Pyrrhotite.

Quartz (SiO_2) is the most important crystalline form of Silicon dioxide. It is a Polymorph and exists in both α and β . The forms stable at ordinary temperatures are referred to as α -forms and those stable at higher temperatures are called β -forms.

In nature α -quartz is found in abundance. Its lattice is trigonal trapezohedral, therefore enantiomorphous and optically active, piezo- and ferro-electric and it makes the plane of polarized light rotate (circular polarization).

Calcite (CaCO_3) or calcium carbonate is one of the oldest known carbonates. It is very common in nature and also very important industrially. It is having a rhombohedral lattice, in which the CO_3^{2-} and Ca^{2+} ions are arranged in a way similar to the rock salt lattice. The CO_3^{2-} ions are all perpendicular to the principal crystal axis, which renders the crystals strongly double refractive. Several other divalent metals are isomorphous with calcite, MnCO_3 and carbonates of manganese, iron, cobalt, zinc and cadmium. These are also found in coal samples.

Kaolinite, Dickite and Nacrite ($\text{Al}_4(\text{OH})_8(\text{Si}_4\text{O}_{10})$) are very commonly found clay minerals in coal. These are usually found together are composed of identical layers, the sequence of which differs slightly. The hardness of clay mineral is very low. The swelling properties are important as the layers can absorb water molecules, organic molecules and other cations. The swollen material is soft and plastic and may lose its crystalline structure and may not have any X-ray reflections. Nacrite and dickite may form larger single crystals but Kaolinite is always fine grained. Clay minerals always contain water and can be abstracted by heat-treatment. A few other minerals in Kaolinite group are Halloysite, Montmorillonite and Bentonite.

Illite ($M_x [Si_{6.8}Al_{1.2}] Al_3Fe_{0.25}Mg_{0.75}O_{20}(OH)_4$) belongs to mica group of layer silicates called as hydro-muscovite. It is similar to muscovite but was initially considered to be a Kaolinite. The layers themselves contain aluminum and the layers themselves contain a usual composition of $AlSi_3O_{10}$. These layers are very strong and elastic. The layers are kept together by hydronium, H_3O^+ ions. It is used for making porcelain material.

2.9 Novel Techniques developed for Dewatering Coal

Researchers have been working on developing novel techniques to dewater fine coal more efficiently. Work has been done to chemically treat coal-water slurries to help dewater fine coals to lower moisture levels. Gehreke, Lyu & Barnhouse (1998) have investigated the use of a reusable ploy (N-isopropylacrylamide) temperature-responsive gel to dewater slurries at low temperature. Gerl & Stahl (1996) have reported the results of the use of steam as an over-pressure forming phase for combined mechanical and thermal dewatering. Guo, Hodges & Uhlherr (1997) have investigated the use of an elevated-temperature mechanical expression process to dewater coal with high moisture content in the range of 60-70%. They were able to dewater 80% of the moisture from the coal. Another work by Dzinomwa, Wood & Hill (1997) reported the use of a super-absorbent polymer which can absorb high quantities of moisture to dewater fine coals. Singh, Besra, Reddy & Sengupta (1998) investigated the use of surfactants (cationic, anionic and nonionic) combined with vacuum filtration. In their study of coal slurries they were able to reduce the moisture content from 21 to 11.7 wt%. A few other methods involving metal ion-surfactants and split size dewatering of coal without addition of any surfactants were studied by Yang, Wang & Parekh (1998). Work is on to continuously

improve the present dewatering techniques such as centrifugation (White et al, 1996) and Vacuum Filtration (Bourgeois & Haque, 2000). In spite of these advances, the coal industry is on the look out for an efficient and reliable dewatering process for the fine coal slurries.

2.9.1 Dewatering Coal using Electromagnetic Waves

In order to dewater coal efficiently and effectively, we have investigated the use of microwave frequencies as well IR frequencies at 3300 cm^{-1} . It has been known that the insulating material can be heated by applying energy to it in the form of high frequency electromagnetic waves (Metaxas & Meredith, 1983). The origin of heating lies in the fact that the electric field polarizes the charges but these polarized charges are not able to follow the rapid reversals of the electric field. Interaction of an electric field with a dielectric has origin in response of charge particle to the electric field. The displacement of these charged particles from this equilibrium position gives rise to an induced dipole. Such induced polarization arises mainly from displacement of electron at the nuclei (electronic polarization) or due to relative displacements of atoms (atomic polarization). In addition to induced dipoles, some dielectrics (polar dielectrics) contain permanent dipoles due to the asymmetric charge distribution of unlike charge partners in a molecule which tend to reorient under the influence of a changing electric field called as Orientation polarization. Finally, another source of polarization arises from charge building up in interfaces between components in heterogeneous systems termed as interfacial space charge or Maxwell Wagner polarization. In a given frequency band, therefore, the polarization vector, P , lags the applied field ensuring that the resulting current, $\partial P/\partial t$, has a component out of phase with the applied electric field which results

in the dissipation of power in the insulating material. At 2.45 GHz, the resonant rotational frequency of a liquid water molecule, the electric field changes direction at the rate of 4.9 billion times per second, which causes rotation of the molecules at the same time. This rapidly alternating electric field exerts a force on the molecule whose resulting violent motion results in instant heating. The power absorbed by a unit volume of a material due to these rapid motions can be written as (Lindroth, 1985, Babu, Farinash & Seehra, 1995) :

$$P = 55.63 \times 10^{-12} |E_0|^2 f \epsilon'', \text{ W/m}^3 \dots\dots\dots (2.5)$$

where E_0 is the intensity of electromagnetic radiation, f is the frequency of the electromagnetic radiation and ϵ'' is the loss factor (imaginary part of the dielectric constant). The advantage of using electromagnetic waves for dewatering coal slurries is based on the fact that ϵ'' for water has sharp peaks at selective frequencies, making P very high at those frequencies. At the microwave frequency $f = 2.45 \text{ GHz}$ ($1 \text{ GHz} = 10^9 \text{ Hz}$), ϵ'' for water is 12 compared to 0.1 for coals making power absorbed by water 120 times larger than that for coal. This is the frequency used for microwave cooking. Similarly at the IR frequency $f = 10^{14} \text{ Hz}$, ϵ'' for water is 30,000 (Irvine & Pollack, 1968) as described later.

Some work has been done on preparation of coal using microwaves. Butcher & Rowson (1988) reported a technique with caustic microwave leach pretreatment prior to conventional dry magnetic separation resulted in a significant increase in the removal of total sulphur. Another paper (Vishwanathan, 1990) reported that microwave heating resulted in increased comminution, partial desulphurization, decomposition of mineral matter and enhanced magnetic susceptibility and beneficiation. Pal, Mukunda &

Mahadevan (1998) have suggested that microwave pre-treatment of coals followed by washing or magnetic separation would facilitate effective and economic beneficiation through selective demineralization. Chatterjee & Misra (1991), in their numerical modeling studies of fine coal drying using microwaves reported power absorption of 337 watts with total incident power of 663 watts (% absorption= 51%) and reported the transient temperature changes with a maximum temperature of 106°C, average temperature of 69°C and a low temperature of 30°C attained during the dewatering process. The use of microwave dewatering of coal samples for laboratory analysis has been reported by Jacobs (1984). In this report the author reported no loss in volatile matter and an increase in the BTU value due to an apparent rank increase due to heating of coal. They also compared results of moisture estimation between microwave and traditional ASTM drying methods and got the same results but with a significant reduction in drying time using microwave technique for western coals. In another publication (Beuerman, 1986) it has been shown that volatile, low molecular weight organics are lost during drying of coal at elevated temperatures as in conventional heating. The author has reported that microwave drying was better than other techniques for moisture determination. The author also concluded that the loss of BTU was higher in the ASTM method as compared to microwave method. In the ASTM method, the weight lost after drying at 107°C for 1½ hour or until constant weight is achieved defines the moisture content. The author also reported the loss of 4-5% of volatile material when the drying temperature was 110°C. The maximum temperature reached during microwave method was reported to be 72°C and constant weight reached in maximum of 16 minutes. Based on this finding microwave drying of coal will reduce the loss of BTU and is a very

rapid drying process. According to Perkin (1980), the dielectric drying (using electromagnetic energy generated at radio and microwave frequencies) results in rapid increase in water temperature due to the selective heating which is not possible in conventional techniques due to the bulk heating of the whole volume of the wet solid.

Lyons, Hatcher & Sunderland (1972) in their investigation for the drying of absorbent materials such as cotton with the aid of microwave heating have reported that rapid mass transfer occurs due to pressure differences caused by the rapid vapor generation throughout the sample. Very small mass and temperature gradients were reported. The authors have also described the drying cycle as divided into four distinct stages- the initial adjustment period during which the temperature throughout the product rises steadily and very little drying occurs; the stage in which liquid is pushed out of the liquid called the liquid movement period; a constant rate of drying followed by a slow rate of drying. Similar work has been done by Harmathy (1969) where they have developed a theory for simultaneous mass and energy transfer which could give the moisture content, temperature, and pressure history of the system. In our effort in this project we try to study the cost effectiveness and the practical validity of the dewatering process using em radiations.

2.10 References

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3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Overview

This chapter gives the details of the samples and instruments used and experimental setup, procedures and the results obtained from the experiments done to understand the dewatering of coal. The experimental results are in the order of TGA and DSC, IR results, microwave results and the results from the lab scale experiments of microwave drying of fine coal slurries. Finally, the identification and quantification of coal slurries using XRD and Rietveld analysis are discussed.

3.2. Experimental

3.2.1. Materials:

Coal samples for the dewatering studies were acquired, in kg quantities, from a preparation plant owned/operated by Consol Inc. These samples were sent to Galbraith Laboratories (Knoxville, TN) for proximate and ultimate analysis, which are given in Appendix II. The most relevant sample for dewatering studies is coal#1 which is the ‘sample sent to settling ponds’, and it contains 52.5% moisture, 26.6% carbon and 15.2% ash. Most of the dewatering experiments were carried out on this sample as the other samples contain only minute amount of moisture. The samples for the XRD quantification of coal were obtained from DTE-Peptec in kg amounts. These samples are pond coal samples which have been treated with the new DTE Peptec technique (News Release, DTE Energy, 2003) developed for cleaning and recovery of ponds coal for

commercial applications. The dry samples used in different experiments were crushed and powdered to make a fine coal sample for the studies.

3.3. Experimental Instrumentation

3.3.1. Thermogravimetric Analysis (TGA)

The moisture loss experiments to investigate the thermal drying process were done using Thermogravimetric Analysis (TGA). The TGA system used is a Mettler Toledo TG 50. It consists of a thermobalance with the furnace controlled by the TA processor. The system can also be used as a very sensitive balance. The amount of samples used were small (mg quantities), in order to have more reproducible results and better analysis. The crucibles used are standard alumina crucible with a capacity of 0.07 ml. Alumina is a very stable material and is completely inert towards most of the materials up to 800 °C. The system was calibrated for temperature and followed a predetermined path during the measurement. The system has the capability of using particular gas environment by purging gas at a desired rate. The system could be used for studies ranging from room temperatures to a maximum of 700 °C. The rate of heating could be set from a minimum of 0.5K/min to a maximum of 50K/min. Lower heating rates (0.5-3K/min) are suggested for higher temperature homogeneity in the samples whereas the higher heating rates are for screening. The system could be used to heat a sample in steps and also could be preset to keep the samples in a fixed temperature for a fixed time (Isotherms). The heating rates can be changed in order to simulate the actual heating process. TG system can be effectively used to study the changes in weight (depicted on the Y-axis) against the temperature changes (shown on the X-axis). The data

can be collected from a computer and processed in other commercial software such as Origin and Excel. The system can be used to find the DTA curves also.

3.3.2. Differential Scanning Calorimetry (DSC)

The Differential Scanning Calorimetry (DSC) experiments were done on a Mettler Toledo DSC 30 system. In DSC, the heat flow to a sample is measured in thermally controlled conditions. In this technique, the material is subjected to a temperature program in which the rate of heat flow is measured continuously. The samples are weighed on the TG balance and placed in a standard aluminum pan with a lid on it. The crucible is then hermetically sealed using a crucible sealing press. An empty pan of similar size with holes on the lid is used as a reference. These two sample holders, sample and reference, are kept at the same temperature by supplying different amounts of electrical power to each holder. The difference in power input is recorded as the heat flow at different temperatures. Thus the difference in amount of energy (heat) absorbed or released by a sample, is compared to the standard reference, as it is heated or cooled. Holes were made on the lid in order for the coal to have free access to the measuring cell atmosphere and for free removal of moisture. The system could be used for studies at temperatures below room temperatures with the use of liquid nitrogen tank attached and could be used for high temperatures in the range of 600°C. The heating rate between 0.5 to 50 K/min was available. The various applications for DSC include determination of melting point temperature and the heat of melting; measurement of the glass transition temperature; curing and crystallization studies; and identification of phase transformations. The system was calibrated so that the heat flow remained on the scale.

3.3.3. Fourier Transform Infra Red (FTIR) Spectroscopy

Fourier Transform Infra Red (FTIR) spectroscopy experiments were performed on Mattson Infinity gold FTIR. This technique measures the absorption of various infrared light wavelengths by the material of interest. These infrared absorption bands identify specific molecular components and structures. An additional unit provided by the MTEC Photoacoustics Inc. was used for the FTIR photoacoustic spectroscopy. Photoacoustic spectroscopy is used for the dense mixture samples which are opaque to the IR rays and thus could not be used for the direct transmission analysis. The working of the photoacoustic unit is based on the photoacoustic signal generated with the incident infrared radiation. When infrared radiation is absorbed by the sample, it is converted to heat within the sample and diffused to the sample surface. This heat is dissipated into the adjacent gas atmosphere which produces a signature signal, specific to the molecules present in the material. The signal generated is processed and the pattern is shown in terms of absorbance or transmittance with difference bands representing the presence of different groups. The samples for study were placed on a sample holder (max size of 10.7mm diameter by 9.0 mm deep) and the sample inserted in the sample chamber where the IR radiation were focused on the sample. The FTIR has another accessory (IR Plan), which could be used for microscopic studies using FTIR but was not used for this work.

3.3.4. X – Ray Diffraction (XRD)

X – Ray diffraction analysis was performed using a Rigaku Diffractrometer (Model D/MAX) and monochromatic radiation of Cu K α lines. This diffractrometer is used to determine the unknown spacing of crystal plane with the known wavelength ($\lambda = 1.5418$

Å) of X – ray and can be performed on either of powder or crystal sample. The other experimental conditions include $\frac{1}{2}^\circ$ divergence and scatter slits, 0.15mm receiving slits, step scan of 0.06° and 30sec counting time at each step, and intensity measured in counts. The voltage applied to the target was set at 40 kV; filament current was set to 30 mA. Sample preparation was done before the XRD data collection. Small amount of sample was filled on the middle of a glass sample holder which was pressed flat to reduce scattering. Thus one or two drops of ethanol were added with the sample and dried in air. After placing the samples vertically in the sample holder and the protective shields closed, the X-rays were turned on using the dedicated computer. The analysis of the X-ray patterns were carried out using Jade software package produced by MDI (Materials Data Inc.) with the JCPDS data files (JCPDS) and ICSD database.

3.4. Experimental Setup

3.4.1. Infra Red Dewatering Setup

For the Infra Red (IR) dewatering experiments, a small IR heating setup was developed for dewatering gram quantities of coal samples. The schematic view of the setup is shown in the Fig. 3.1. A commercial electric IR heater (F-Series, Solar Products Inc.) was used for the setup. The dimensions for the heater are 6inch x 6inch with a watt density of 25Watt/inch^2 . The heater is a TYPE-B heater or a medium wave length heater with wavelength output in the 4-6 microns range and is inversely proportional to heater temperature i.e. with the increase in temperature the wavelength decreases. The energy output from the heater is not precise at a particular frequency. The peak frequency is described by the heater temperature with some energy output at other frequencies.

(Website, Solar Products, Inc., 2005). The heater consists of a hole for a thermocouple to be placed inside the thermowell. We used a K-type (Alumel-Chromel) thermocouple connected to the temperature controller (Omega Inc.). The heater could be set at a particular temperature using the temperature controller to give energy output at a desired wavelength.

Figure 3.1: Schematic view of the IR dewatering Setup

The schematic view of the IR heating setup with the heater and glass plate for holding the sample is shown.

3.4.2. Microwave Experimental Setup

For the investigation of selective heating using microwave radiation, we did experiments of gram quantities of coal. These experiments were carried out with a conventional microwave oven (GE Model JES838SH001) with maximum power of 800 Watts. To measure the power used in the experiments, a power meter was inserted in the circuit between the power outlet and the microwave oven. In the first set of experiments, the sample was heated for 10-seconds intervals followed by measuring the weight of the

samples and recording the power used. In the other experiments, the interval was changed to 30-seconds.

In the second stage of experimentation, we designed a laboratory-scale microwave dewatering unit with a conveyor-belt feed system to simulate a potential commercial unit. Pictures of this laboratory dewatering unit are shown in Fig. 3.2 and schematic diagram of this unit is shown in Fig. 3.3.

Figure 3.2: Pictures of the Laboratory scale microwave conveyor belt dewatering unit

(A) The complete unit covered with the microwave shielding is shown. (B) close up of the unit without the shield showing the microwave and the feeding belt.

The microwave dewatering unit consists of a store-bought 800 watt microwave oven whose two opposite sides were opened up for feeding a conveyor-belt. The conveyor belt used is a commercially sold conveyor belt (Taconic TFE-Glass TM) primarily used in the food industry.

Figure 3.3: The schematic view of the laboratory scale microwave dewatering unit

This belt is made up of Teflon material and optimum for high temperature use. The belt has a non metallic splicing (fabric notch) and thus not affected by the microwave radiation and also has a moisture resistant coating. Thus this belt was considered optimum for the lab scale dewatering application. The complete specifications for the belt can be found on the website of the company (Website, Taconic, 2005). We used a conveyor belt 6 inches wide for the construction of the unit. The conveyor-belt is fed by two motor driven rollers mounted at the end of the table. The feed-speed is controlled by the rotation speed of the rollers. Due to the radiation hazard because of the open microwave oven, we used a commercial shield (Diamond Manufacturing) for safeguarding the system as well as to allow a visual view of the system during operation. This perforated metal shielding is made up of aluminum. The shielding is 99% effective

for frequencies up to 7GHz (Website, Diamond Manufacturing, 2005). A portable microwave detector (MD 2000 microwave leak detector) was used to check for any leaks of the microwaves outside the apparatus. The recommended permissible levels of RF radiation exposure are less than 5 milliwatt/square centimeter (OSHA Safety Code 6, 1987). Since the operator of the system must be protected from any microwaves, an electrical circuit was designed to control the operation of the system from a distance. A basic design of this electrical system for the microwave unit is shown in Fig. 3.4 and for the control system in Fig. 3.5. The main consideration in this design is that with the remote control switch, power to the microwave oven and the conveyor-belt motor can be controlled.

Figure 3.4: The basic design of the electrical system used in the laboratory scale microwave dewatering unit.

Figure 3.5: The electric system used for the remote controlled operation of the laboratory scale microwave dewatering unit.

3.6. Results and Discussions

3.6.1. TGA and DSC results

The moisture loss using thermogravimetric analysis (TGA) on different coal samples is shown in figs.3.6-3.9 for different sample sizes and heating rates. TGA is a good technique to estimate the amount of moisture in coal samples and also is similar to conventional or thermal heating. The weight loss in Figs. 3.7 and fig. 3.8 is for the ‘coal before processing’ and ‘coal sent to power plants’. These results are for room temperature to 250°C. These samples show continuous weight loss beyond 100°C as expected in dewatering process. This continued weight loss may be due to the loss of volatile matter from coal at higher temperature as explained by Beuerman (Beuerman, 1986) and due to oxidation of coal. The amount of weight loss till 100°C is less than 2% which is in agreement with the moisture content in these coal samples as noted in Appendix I.

Figure 3.6: Results from the TGA on the (A) coal before processing and (B) Coal sent to power plant.

TGA results with the Y axis shows the % weight loss vs. temperature in °C. The results shown are for four different sample sizes and the heating rate for the experiment was 10°C.

In order to check for the effect of repeated heating of coal we repeatedly ran TGA on ‘coal sent to power plants’ to completely remove moisture from coal. After the first TGA, this sample was left in air overnight and again a TGA was run the next day. The results of this experiment are shown in Figure 3.7.

Figure 3.7: Results from the TGA on the coal sent to power plants for moisture retention after initial dewatering of moisture and effect of repeated heating.

TGA results with the Y axis shows the weight loss vs. temperature in °C. The results shown are for an initial sample size of 49.5 mg. The sample was heated in TGA and kept overnight in air and then again heated next day for a 2nd run and for a 3rd run.

The weight loss for the 1st run is similar to explained previously with increase in weight at higher temperatures. For the second run the weight loss is comparatively less but follows a similar pattern as the first run. We assume that the weight loss till 100 °C (<1%) is due to moisture reabsorbed by the coal, which is negligible. But for the third run, the initial weight is greater than the starting weight which signifies that some irreversible changes have taken place due to repeated heating of coal samples.

In Fig. 3.8, TGA results for weight loss on different sample sizes of the ‘Samples sent to Coal’ are shown and Fig. 3.9 where the moisture loss in TGA for different heating rates for the same coal samples are shown. The weight loss is primarily due to loss of moisture since most of this loss occurs for $T \leq 100\text{ }^{\circ}\text{C}$, and it agrees with the % moisture given in Appendix 1. In Fig. 3.8, as the amount of samples increases the temperature at which complete dewatering is achieved increases. In Fig 3.9, at lower heating rates the moisture removal is at lower temperatures and as the heating rates increased the moisture removal point is drifted beyond $100\text{ }^{\circ}\text{C}$. This is expected from a conventional heating process and the shift in the inflexion point may be due to the heat flow problems in coal.

Figure 3.8: Results from the TGA on the ponds coal for different weights.

TGA results with the Y axis shows the % weight loss vs. temperature in $^{\circ}\text{C}$. The results shown are for three different sample sizes of 50mg, 100 mg and 200mg and a heating rate of $3\text{ }^{\circ}\text{C}$. The result shows the drifting of the inflexion point to a higher temperature for a larger mass.

These TGA results on “Samples sent to ponds” emphasize that the conventional drying is slow and the rate is limited to by the rate of conductivity as only the surface is heated. In this kind of drying there is an internal resistance to the heat flow due to low thermal conductivity and the large overall dimension of the wet coal which causes the

surface temperature to reach that of the adjacent air stream, so reducing the heat flow to the solid and creating significant temperature gradient.

Figure 3.9: Results from the TGA on the ponds coal for different heating rates.

TGA results with the Y axis shows the % weight loss vs. temperature in °C. The results shown are for three different heating rates (β) of 3 °C/min, 10 °C/min and 20 °C/min for approximately 100mg coal sent to ponds samples. Horizontal lines for different dewatering levels, 60%, 70% and 80% and then taking X- axis intercepts for these intersection points as the absolute temperatures for respective dewatering level for the calculation of activation energies.

TGA can also be used to calculate the Activation energy (E_a) of the dewatering process. In accordance with the Flynn-Wall method for a constant weight loss (Flynn & Wall, 1966), we determine the temperatures for a constant weight loss for different heating rates as shown in fig 3.9. A horizontal line for different moisture level (60%, 70% and 80% moisture level) is drawn and vertical lines from the intersection of those weight loss and the dewatering thermograms is used to find the temperatures for each heating rate. In Figure 3.10, $\log \beta$ vs. $1/T$ values are plotted. Using the slopes in Figure 3.10 and

equation 3.1, we can calculate the activation energy for dewatering process. The procedure is repeated for three values of moisture content to test the consistency of the method.

$$E_a/R = -d(\ln\beta)/d(1/T) \dots\dots\dots (3.1)$$

Where E_a is the activation energy, R is the gas constant (8.314 J/K-mol), β is the heating rate and T is the absolute temperature in °K.

Figure 3.10: Plot of $\log \beta$ vs. $1/T$ for three different moisture levels.

Results with the Y axis showing $\log \beta$ vs. $1/T$ in °K. The data is obtained using figure 3.9 for three different weight % levels-60%, 70% and 80%.

Using the above equation and the slopes we get the activation energy $E_a=8.9$ kilocalorie/mole. The expected value for dewatering is about 9.7 kilocalorie/mole. Thus this confirms the fact that for higher moisture content samples, by heating the coal we are essentially removing moisture from the coal. TGA is used for the later experiments to determine the initial moisture present in the coal samples used for the various experiments.

In Figure 3.11, results for DSC on coal sent to ponds for different heating rates are shown. The Y-axis shows the heat flow (a –ve values meaning an endothermic process) vs. temperature. Three different stages of the heating process are evident from the DSC data. There is an initial phase of heat adjustment phase till around 35 °C followed by a constant increase in the heat input for raising the temperature of the sample and then finally a rapid increase of heat input relating to latent heat of vaporization and actual removal of water around 100 °C . For the 5 °C/min heating rate the peak heat input is around 85 °C and for 10 °C/min the peak is around 100 °C. The area under the DSC curve gives the energy input for the dewatering process and it is clear that increasing the rate of dewatering by a conventional process is not economical as in order to double the rate, the area has gone up by a factor of about 2.5 and the inflexion point has shifted towards the right. This again confirms the ineffectiveness of the conventional heating process as a quick and efficient method of dewatering coal.

Figure 3.11: Results from the DSC on the ponds coal for different heating rates.

DSC results with the Y axis showing the amount heat absorbed vs. temperature in °C. The results shown are for two different heating rates: (a) 3 °C and (b) 10 °C for the same amount of sample.

3.6.2. IR Experiments

In order to investigate the effectiveness of IR dewatering FTIR was run on Ponds coal sample. The result for this is shown in Figure 3.12. The spectrum obtained using an FTIR is typical to the elements present in the sample. In the spectrogram, the broad peak around is due to the presence of moisture and high absorbance shows that IR is being absorbed effectively. To further investigate the effectiveness of energy absorption in the IR region, a plot of absorption coefficient for water (k) vs. the frequency of radiation is plotted using the data from Irvine et al (Irvine & Pollack, 1968). The plot is shown in Figure 3.12. The figure shows sharp peaks in the frequency regions of IR especially around 10^{14} Hz and a band just above 10^{13} Hz. Thus this shows that water will absorb more energy in the IR region than coal for heating coal water slurry.

Figure 3.12: Plot of absorption coefficient (k) vs. frequency.

Plot shows Absorption coefficient (k) on the Y-axis vs. Frequency (on a logarithmic scale) on the X-axis for the IR frequency range.

We know, according to the black body radiation, as the temperature of body increases, the amount of energy emitted in the visible radiation increases. The emission

spectrum is called black-body spectrum. The Planck's radiation law (equation 3.2) gives the relation between the power emitted per unit area of a black body (I_λ), wavelength of the radiation and the absolute temperature.

$$I_\lambda = (2\pi c^2 h / \lambda^5) * (1/e^{hc/\lambda kT} - 1) \dots\dots\dots (3.2)$$

where I_λ is the power emitted per unit area, c is the velocity of light, h is the Planck's constant, k is the Boltzman's constant and T is the absolute temperature.

In equation 3.2 replacing $\lambda=c/v$ and placing the values for the constants we get a simplified equation in terms of frequency of the radiation:

$$I_v = 4.626 * 10^{-47} * v^3 * (1/e^{(4.8 * 10^{-11} * v/T)} - 1) \dots\dots\dots (3.3)$$

Where, I_v is the power emitted per unit area, v is the frequency of the radiation and T is the absolute temperature

Using equation 3.3 and placing the values of v and T , we have plotted the power emitted per unit area of a black body (I_v) vs. frequency as shown in figure 3.12.

Figure 3.13: Plot showing the power emitted per unit area of a black body (I_v) vs. the frequency of the radiation for different temperature.

The plot between the powers emitted per unit area of a black body (I_v) vs. frequency for different set temperature based on the Plank's radiation law (equation 3.3).

From figure 3.13, it is observed that the total power emitted (area under a curve) increases rapidly with temperature and the peak intensity moves towards higher frequency (shift of the peaks towards right). This implicates that the use of IR heaters is only favorable at higher temperature ranges of the IR source. Different set temperature of the IR source relate to a particular frequency. A wave length of 6 microns relates to a temperature of around 250 °C. Thus any temperatures below 250 °C are not feasible for industrial applications.

Using the IR setup, with different set temperature of 250 °C, 350°C and 450°C for the Ponds coal dewatering experiments were done. The results are shown in figure 3.14. The samples were placed in a clay dish. The samples (17-19 grams) were IR treated for 3 minutes interval, taken out and weighed for the moisture loss and again treated till a constant mass achieved.

Figure 3.14: Results for the IR heating of the coal sent to ponds.

Results with the Y axis shows the % weight loss vs. time in minutes for the IR heating of coal sent to ponds. The sample size was around 20 grams and the set temperature for the heater varied to 250 °C, 350 °C and 450 °C.

For the set temperature of 450°C, the dewatering is achieved in about 20 minutes and for 250°C in approximately 40 minutes. As per figure 3.13, at higher temperature the energy radiated from a body is higher but higher source temperatures also correspond to higher temperature to which the coal is subjected. We measured the temperatures at the base of the setup where the coal samples were placed for different set temperature of the source. The results are shown in Table 3.1.

Table 3.1: Temperature at the base (near sample) for different source temperature

Full Brick Distance (9 inches)		Half Brick Distance (4.5 inches)	
Set Point	Temperature at Base	Set Point	Temperature at Base
200 °C	30 °C	200 °C	75 °C
300 °C	38 °C	300 °C	130 °C
400 °C	50 °C	400 °C	152 °C
500 °C	64 °C	500 °C	-
600 °C	75 °C	600 °C	-
700 °C	94 °C	700 °C	-
800 °C	110 °C	800 °C	-
900 °C	135 °C	900 °C	-

Table shows the temperature at the base of the IR heating setup due to different set temperature of the heater. First column is when the IR heater is at a full length distance and the second for half brick distance.

For half brick distance (4.5 inch) for which the experiments shown in figure 3.14, a temperature of 152°C is achieved for set temperature of 450°C. We assume that if the coal samples are exposed to higher temperature than that for such extended period of time, irreversible changes will take place as explained previously in the TGA results administered in conventional heating. Thus higher temperatures for the heater were not investigated. Though theoretically IR seems to be an effective technique to dewater coal, we didn't find it very exciting practically. The heater takes around 7 minutes to reach to a temperature of 450°C and the dewatering is achieved in around 20 minutes, thus IR heating is not a very efficient and fast dewatering process.

3.6.3. Microwave Heating Experiments

In the next set of experiments we tried to look into the effectiveness of radiation at microwave frequencies for dewatering experiments. The samples were placed on a flat Styrofoam plate as a thin layer so that maximum use of the power could be exploited. There is no visual indication of any water being absorbed by the Styrofoam plate. The samples were heated for different time intervals followed by measuring the weight of the samples and recording the power used. The procedure was followed till there was no further reduction in weight.

In figure 3.15, the sample was heated for 10-seconds intervals followed by measuring the weight of the samples and recording the power used and in figure 3.16, sample was heated for 30-second interval. The rate of moisture loss, which eventually reaches 50%, is the largest for the smallest initial mass as expected. The results shown are for four different samples sizes of 50 grams, 100 grams, 150 grams and 200 grams.

Figure 3.15: Results from the microwave heating on the ponds coal for different sample sizes for 10 second interval.

Microwave heating results with the Y axis shows the % weight loss vs. time in minute. Weight loss (left scale and open symbols) and power consumed (right scale and closed symbols) as a function of time in the microwave dewatering of a wet coal for four different masses

Figure 3.16: Results from the microwave heating on the ponds coal for different sample sizes for 30 second interval.

Microwave heating results with the Y axis shows the % weight loss vs. time in minute. Weight loss (left scale and open symbols) and power consumed (right scale and closed symbols) as a function of time in the microwave dewatering of a wet coal for four different masses.

The slope of the initial mass loss probably represents the loss of “free water”, whereas the slower rates at larger times are due to the release of “bound water” contained in the pores of the coal structure.

Figure 3.17 shows a comparison of the three different heating processes viz. Conventional (thermal) heating, IR heating and microwave heating for %weight loss with respect to time was taken for the three processes. Roughly the same amount of sample (≈ 20 grams) was used for the three processes for a better comparison. For conventional heating the coal was taken in a glass dish and kept in an oven, with air flow to take away the moisture removed, at a fixed temperature of 110°C and taken out every 30 sec interval to weigh it. For the IR setup, the temperature for the heat controller was set at a temperature of 350°C and the sample placed in a pottery dish. The sample was taken out every minute and weighed for moisture loss. The microwave process was used as described earlier. The Microwave heating process is found to be the quickest (complete dewatering attained in less than 10 minutes) and the conventional heating is the slowest taking a lot of time to dewater completely. The IR heating took around 25 minutes to completely dewater the coal samples. Based on these results, we concentrated our efforts towards the use of microwaves to dewater coal as they seemed to be the most efficient.

In order to determine whether microwave heating has in any way affected the coal or ash in the sample, we used X-ray diffraction of the ‘before’ and ‘after’ sample from the experiments in Fig. 3.17. The x-ray diffraction patterns (Fig. 3.18) show very minor changes only in the intensity and no change in the pattern signifying that chemical phases in the ash are not affected by microwave heating. The broad background peaks near $2\theta \approx 25^{\circ}$ is due to coal carbon, indicating that carbon is still intact after microwave

treatment. This is an important advantage of microwave dewatering vis-à-vis thermal drying of coals

Figure 3.17: Comparison of three different heating processes viz. conventional, IR and microwave.

Results of different heating processes in terms of the % weight loss vs. time in minute. For the conventional heating, samples were heated in an oven set at 110 °C, for the IR the heater was set at 350 °C. The sample size used for the three processes is 20 grams.

Figure 3.18: Results from the XRD on the ponds coal for samples 'before' and 'after' microwave treatment.

XRD results with the Y axis showing the Intensity of the signal (arbitrary units) vs. 2 theta values. The results shown are for samples before microwave treatment and after microwave treatment.

Since coal is a highly porous substance, we compared its dewatering process under microwaves, against that in a sponge, which is also a porous material. The sponge was kept in water over-night before microwave treatment for moisture removal. The results are shown in Figure 3.19. The dewatering curve for sponge is quite linear where as the dewatering curve of coal shows the different phases of initial adjustment, quick moisture removal and in the end a slower rate of moisture removal. This difference in the dewatering curve could be explained by the fact that the moisture in the sponge is just physically attached where as moisture in coal is attached with hydrogen bonds as explained in the previous section (Forms of water in coal). Equal quantities of water and coal sent to ponds were also heated in the microwave oven and compared. The results are shown in figure 3.20. The slope for water is higher than that of coal which is expected. This difference could be attributed due to some loss of energy to coal and energy lost in pushing the water out of the capillaries.

Figure 3.19: Comparison of microwave treatment for Coals sent to ponds and a presoaked sponge.

Comparison of the microwave heating of Ponds coal sample and a presoaked sponge with Y- axis showing the % weight loss vs. the dewatering time in minutes. About 25 grams of the coal sample was used.

Figure 3.20: Comparison of microwave treatment of equal quantities of coal sent to ponds and water.

Drying curves for coal and water under microwave heating with Y- axis showing the % weight loss vs. the dewatering time in minutes.

In Figs 3.15 and 3.16, we obtained the power needed to essentially eliminate all moisture (inflexion points in the figures which are near 53% weight loss). This power is plotted against the mass of the sample used in Fig 3.21. The linear relation obtained is according to expectations, with the intercepts close to zero mass yielding small amount of power utilized by the coal sample (power lost to the plate, coal and unused power). The slope $dP/dm \cong 1.33 \times 10^{-3}$ kWh/gm for 10-seconds heating and $dP/dm \cong 9.8 \times 10^{-4}$ kWh/gm for 30-second heating is obtained. Assuming the same dewatering rate for larger masses of wet coal, we calculate that 1kWh of power should be able to vaporize 0.75 kg of water ($1/1.33 \times 10^{-3}$) for 10-second heating and 1.02 kg of water ($1/9.8 \times 10^{-4}$) for 30-second heating.

Figure 3.21: Power required for removing moisture vs. sample size.

Power used for dewatering is plotted against the initial mass of the sample with 53% moisture for two heating intervals using inflexion points from figure 3.15 and 3.16. The dotted lines are drawn to estimate the slopes dP/dm .

3.7. Theoretical Estimate

Energy H needed to convert ' m ' grams of water at room temperature (25°C) to steam at 100°C is given by

$$\begin{aligned}
 H &= m\{(100-25)(4.18)+2256\} \text{ Joules} \\
 &= 2.5692 \text{ m kilojoules} \quad \dots\dots\dots (3.4)
 \end{aligned}$$

For $m = 1 \text{ kg}$, equation 3.4 gives $H = 2.5692 \times 10^6 \text{ J}$. Since $1\text{kWh} = 3.6 \times 10^6 \text{ J}$, this gives $H = 0.71 \text{ kWh}$ for one kg of water. Conversely 1kWh of power is able to vaporize 1.40 kg of water. In Figs 3.15 and 3.16, the initial flat region of the curves is most likely due to the power used to heat the water from 25°C to 100°C whereas the sharp slope indicates conversion to steam. If we neglect the former contribution, then $H = 2.256 \times 10^6 \text{ J}$ for 1 kg of water or conversely one kWh of power is able to vaporize 1.02kg of water. Comparing the experimental and the theoretical values, we get an efficiency of about

73% for the dewatering process using microwave. The significance of this is that by using microwave power, the efficiency of dewatering obtained in our experiments is quite close to the theoretical limit. Thus most of the power is being used to dewater the coal, with only negligible loss of power to coal or surroundings. These experiments suggest dewatering of coals by microwave heating is extremely efficient and hence a practical possibility.

For further investigating these results, we did experiments using the microwave dewatering conveyor belt unit using larger sample sizes. Known amounts of samples were spread evenly over the conveyor belt which was fed through the microwave unit at a fixed speed. A power meter was inserted in the line to know the amount of energy being used for the dewatering process. For the variables in the present setup, like the power, size of the cavity, feed time in the setup, it was determined that the optimum belt speed is about 12 in/min (see Fig. 3.22).

Figure 3.22: Power consumed and belt speed vs. % moisture lost used to determine the optimum belt speed

The power consumed is shown on Y-axis (left) and the Belt speed Y-axis (right) vs. % moisture lost. The optimum belt speed is around the 50% moisture point for a belt speed of 12 inch/min (shown by arrows).

For this belt speed we determined that 1.16 kg water/kWh could be removed. Comparing this value with the theoretical value of 1.4kg water/kWh we get an efficiency of 83%. This increase in efficiency from the previous experiment may be due to the fact that larger quantity samples are used thus reducing the lost power and the samples are more spread out on the conveyor belt.

Cost Estimate: We next estimate the cost of dewatering a ton (10^6 grams) of coal having 10% moisture (10^5 grams). Assuming one kWh is consumed to eliminate 1.4 kg of water, this would require 71.4 kWh for one ton of coal. At 0.04 \$/kWh, yields the cost of dewatering to be about \$3/ton of coal with 10% moisture. This estimate reflects only the cost of power used at the rate indicated.

3.8 Identification and quantification of coal

A lot of wastes are relegated to the settling ponds with the finer fractions of coal. The slurry is a mixture of water, clay particles, coal fines and sand. In order to make the coal present in the settling ponds commercially viable, it is very important to identify the different minerals present with the coal and then remove them to bring the coal to the required standards. XRD was used on various coal samples provided by DTE Peptec to identify the various mineral phases present. Figure 3.23 shows typical XRD spectra for three different coal samples. Using the JCPDS library (JCPDS), the five major minerals present in the sample are Quartz, Pyrite, Calcite, Kaolinite and Illite. At first glance, the lines from the different minerals appear hopelessly intermixed for any quantitative determination of the minerals. However the two lines near $2\theta \approx 8^\circ$ and $2\theta \approx 12^\circ$, respectively due to Illite and Kaolinite, are well separated from the other lines. These lines are used here to determine the ratio K/I (Kaolinite/Illite). Since the intensity of XRD

lines depends upon the mass of the sample exposed to X-rays (among various other factors), a quantity difficult to control from sample to sample, the ratio K/I can be determined more accurately than the individual components. Even for the ratio K/I, a calibration curve is needed which then can be used for the unknown samples.

Figure 3.23: Room temperature X-ray diffraction patterns of the three coal slurries. Expected line positions due to the listed minerals are indicated.

The plot shows XRD analysis for the three coal samples viz southpit coal west, mid and east. The different peaks are identified and the number corresponding to the particular peak is written besides it.

The calibration curve of the ratio of the intensities of the two peaks against the ratio of weight percentages of K/I is shown in Figure 3.24. For developing this curve, we used commercial Kaolinite (Fisher Scientific) and Illite (Wards Scientific) samples and the intensities represent the areas under the peaks near $2\theta \approx 8^\circ$ and $2\theta \approx 12^\circ$. The relatively good linear curve of Fig.3.24 provides good confidence in the procedure. In Table 3.2, we have listed the intensity ratio $m=K/I$ determined for the three samples using the calibration curve of Fig. 3.24. The fact that the calibration curve does not quite go

through the origin is because the Kaolinite and Illite samples are only about 95% pure; the rest being impurities of each other.

Of the five minerals present in these samples (Fig. 3.23), only Illite $((K,H_3O)Al_2Si_3AlO_{10}(OH)_2)$ and Kaolinite $(Al_2Si_2O_5(OH)_4)$ contain Aluminum. Therefore the percentage 'n' of Aluminum present in the samples must be due to these two minerals. These percentages of Al, determined from the standard AA (Atomic Absorption) spectroscopy, are also listed in Table 3.2.

Figure 3.24: Plot of the XRD intensity ratio for the lines at $2\theta \approx 12^\circ$ for Kaolinite (K) to the line at $2\theta \approx 8^\circ$ for Illite (I) against the ratio of the weights of K/I using standard samples.

The solid line is the least-squares fit through the points with the correlation coefficient $R=0.992$. For each point the error levels are shown error bars.

Let x and y be the weight percentages of Kaolinite and Illite respectively in the samples. Using the molecular weights (MW) of Kaolinite = 258.16 and that of Illite = 398.31, then it follows that

$$0.209x + 0.203y = n \quad \dots\dots\dots (3.5)$$

and $x/y = m \quad \dots\dots\dots (3.6)$

Here the factors $0.209 = 2(27)/258.16$ and $0.203 = 3(27)/398.31$ represent the percentages of Al in Kaolinite and Illite respectively. Solving for y using equations (3.5) and (3.6) yields

$$y = n/ (0.209m + 0.203) \quad \dots\dots\dots (3.7)$$

Using the experimental values of n and m and Equations (3.6) and (3.7), x and y, representing respectively the percentages of Kaolinite and Illite, can then be determined. For the three samples used in this work, these magnitudes are listed in Table 3.2. The listed values correspond to weight percentages in the coal samples on a dry basis. The carbon present in the coal does not interfere with this analysis since in the XRD patterns (Fig. 3.23), the broad peak due to carbon is centered around $2\theta \approx 25^\circ$, far from the two lines used in the analysis here. To completely remove the effects of coal on the analysis, the same analysis could be carried out on the ash of the samples after burning off the carbon in the standard proximate analysis of the coal. In the three samples used in the analysis here, the weight % of ash is nearly 40%.

Table 3.2: Parameters for the three coal slurries as described in the text. The numbers in () represent experimental uncertainties of the quantities in the last decimal place.

Sample	XRD Peak ratio of K/I	m = K/I	n (% of Al)	Kaolinite (wt %)	Illite (wt %)
Southpit coal (West)	2.35	0.60 (3)	4.5 (1)	8.2 (5)	13.7 (5)
Southpit coal (East)	1.42	0.33 (3)	4.3 (1)	5.2 (5)	15.8 (5)
Southpit coal(Middle)	2.04	0.51 (3)	4.1 (1)	6.7 (5)	13.2 (5)

An alternative procedure for the quantification of the minerals using XRD patterns is using the Rietveld analysis (Bish, Howard, 1988; Rietveld, 1969). As explained earlier, in this method, the observed XRD patterns are compared with the simulated patterns using the percentages of the minerals as the fitting parameters. The output of the results of the Rietveld quantitative analysis and the simulated curves are shown in the appendix. The results of the analysis are shown in Table 3.3. The % ash content of each sample is also shown in Table 3.3. The XRD quantitative analysis shows the result for all the crystalline phases present with very good “goodness of fit ratio” values of 0.95, 1.05 and 1.06 for Southpit coal-west, east and middle respectively. The ash content of the coal comprises the crystalline phases. Thus these numbers obtained need to be factored for the ash content. The results for the corrected values are also shown in Table 3.3. These results are close to the Kaolinite and Illite percentages obtained using the standard XRD/AA procedure.

Table 3.3: Ash content and the Kaolinite and Illite % values from Rietveld software before and after correction for ash content

Sample	% Ash content	Data received from Rietveld software		Data corrected for the ash content	
		Kaolinite (wt %)	Illite (wt %)	Kaolinite (wt %)	Illite (wt %)
Southpit coal (West)	38.3	19.0	46.0	7.3	17.6
Southpit coal (East)	41.13	19.4	46.3	7.9	19.0
Southpit coal(Middle)	41.24	20.0	39.8	8.2	16.4

3.9 References

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4. CONCLUSIONS AND FUTURE DIRECTION

4.1 Summary and Conclusions

Dewatering of fine coal slurries using microwave heating at 2.45 GHz and IR heating for frequencies around 10^{14} Hz has been studied using various techniques, modeling and experimentation. Though IR heating was found to be more efficient than the conventional heating, still it has some problems for its application for coal dewatering. Experiments have shown that the carbon in coal is not affected by microwave treatment and microwave heating was found to be a very quick and efficient method of dewatering fine coal slurries as compared to IR heating. Experiments have shown that with the use of microwave heating efficiency of dewatering approaching the theoretical limit is possible.

Experiments on gram quantities of coal were done in a commercial microwave oven. The microwave treatment did not result in problems like self ignition or any physical change. Complete dewatering using microwave heating was achieved in less than 14 minutes in all the experiments. Longer duration of microwave irradiation was found to be more efficient than very small intermittent heating periods in pulsed microwave heating. A laboratory scale conveyor belt unit simulating a commercial system was constructed and tested with appropriate shielding and remote control. This helped to demonstrate a possible commercial application. Using the experiments, dewatering efficiency of about 83% is achieved. A cost estimation for dewatering of a ton of fine coal slurry containing 10% moisture, at 0.04 \$/kWh, yields the cost of dewatering to be about \$3/ton of coal. Adoption of such an approach for industrial

application depends upon the economics of the coal market, a subject beyond the scope of this work.

XRD studies were also used for the identification and quantification of various coal samples. Rietveld software was used for the quantification of coal samples. A method for quantifying Kaolinite and Illite in samples of fine coal slurries is described. The method, combining X-ray diffraction and atomic absorption spectroscopy, was successfully applied for the determination of weight percentages of Kaolinite and Illite in three samples of fine coal slurries. Close agreement between this theoretical method and the Rietveld technique is observed.

4.2 Future Work

We investigated the effects of microwave on dewatering using a lab-scale conveyor belt setup and found the process to be efficient and effective. A scale up of this unit with larger quantities of coal slurry samples could be studied. An automatic feeder which feeds the conveyor belt could be used for the work. Higher power of microwave irradiation would be required and can be provided by multiple microwave sources and using wave guides to focus the microwaves on the conveyor belt. This will ensure higher efficiency due to proper distribution of energy. A magnetic separator could be incorporated in the system to clean the ash from the coal slurries. These dewatered coals could be studied using the XRD analysis variation in composition. The effect of irradiation time and varying magnetic field on the final coal heat content could be studied. A combined microwave and mechanical dewatering process like centrifugation or vacuum filtration could also be simulated.

Appendix-I

The standard sieve designation, alternate designation and nominal sieve opening.

sieve designation standard	sieve designation alternate "mesh"	nominal sieve opening (in.)	nominal wire diameter (mm)
125 mm	5	5	8
106 mm	4.24	4.24	6.3
100 mm	4	4	6.3
90 mm	3 1/2	3.5	6.3
75 mm	3	3	6.3
63 mm	2 1/2	2.5	5.6
53 mm	2.12	2.12	5
50 mm	2	2	5
45 mm	1 3/4	1.75	4.5
37.5 mm	1 1/2	1.5	4.5
31.5 mm	1 1/4	1.25	4
26.5 mm	1.06	1.06	3.55
25 mm	1	1	3.55
22.4 mm	7/8	0.875	3.55
19 mm	3/4	0.75	3.15
16 mm	5/8	0.625	3.15
13.2 mm	0.53	0.53	2.8
12.5 mm	1/2	0.5	2.5
11.2 mm	7/16	0.438	2.5
9.5 mm	3/8	0.375	2.24
8 mm	5/16	0.312	2
6.7 mm	0.265	0.265	1.8
6.3 mm	1/4	0.25	1.8
5.6 mm	No. 3.5	0.223	1.6
4.75 mm	No. 4	0.187	1.6
4 mm	No. 5	0.157	1.4
3.35 mm	No. 6	0.132	1.25
2.8 mm	No. 7	0.11	1.12
2.36 mm	No. 8	0.0937	1
2 mm	No. 10	0.0787	0.9
1.7 mm	No. 12	0.0661	0.8

sieve designation standard	sieve designation alternate "mesh"	nominal sieve opening (in.)	nominal wire diameter (mm)
1.4 mm	No. 14	0.0555	0.71
1.18 mm	No. 16	0.0469	0.63
1 mm	No. 18	0.0394	0.56
850 mm	No. 20	0.0331	0.5
710 mm	No. 25	0.0278	0.45
600 mm	No. 30	0.0234	0.4
500 mm	No. 35	0.0197	0.315
425 mm	No. 40	0.0165	0.28
355 mm	No. 45	0.0139	0.224
300 mm	No. 50	0.0117	0.2
250 mm	No. 60	0.0098	0.16
212 mm	No. 70	0.0083	0.14
180 mm	No. 80	0.0070	0.125
150 mm	No. 100	0.0059	0.1
125 mm	No. 120	0.0049	0.09
106 mm	No. 140	0.0041	0.071
90 mm	No. 170	0.0035	0.063
75 mm	No. 200	0.0029	0.05
63 mm	No. 230	0.0025	0.045
53 mm	No. 270	0.0021	0.036
45 mm	No. 325	0.0017	0.032
38 mm	No. 400	0.0015	0.03
32 mm	No. 450	0.0012	0.028
25 mm	No. 500	0.0010	0.025
20 mm	No. 635	0.0008	0.02

Appendix II

Results of the proximate and ultimate analysis on the four coal samples.

SAMPLE ID	ANALYSIS	AS RECEIVED		DRY BASIS	
SAMPLES SENT TO PONDS	Loss on Drying	52.53	%		
	Carbon	26.59	%	56.01	%
	Hydrogen	6.50	%	1.31	%
	Nitrogen	<0.5	%	<0.5	%
	Sulfur	1.42	%	2.99	%
	Chlorine	230	ppm	485	ppm
	Ash	15.23	%	32.08	%
	Oxygen (by diff)	50.24	%	7.56	%
SAMPLES MAGNETICALLY SEPARATED	Loss on Drying	16.88	%		
	Carbon	3.44	%	4.14	%
	Hydrogen	1.49	%	<0.5	%
	Nitrogen	<0.5	%	<0.5	%
	Sulfur	0.33	%	0.40	%
	Chlorine	160	ppm	193	ppm
	Ash	68.03	%	81.85	%
	Oxygen (by diff)	26.69	%	14.07	%
COAL AS MINED	Loss on Drying	0.71	%		
	Carbon	62.74	%	63.19	%
	Hydrogen	4.57	%	4.52	%
	Nitrogen	1.10	%	1.11	%
	Sulfur	4.46	%	4.49	%
	Chlorine	489	ppm	493	ppm
	Ash	18.29	%	18.42	%
	Oxygen (by diff)	8.79	%	8.22	%
COAL SENT TO POWER PLANT	Loss on Drying	1.12	%		
	Carbon	75.74	%	76.60	%
	Hydrogen	5.46	%	5.40	%
	Nitrogen	1.37	%	1.39	%
	Sulfur	3.17	%	3.21	%
	Chlorine	637	ppm	644	ppm
	Ash	6.21	%	6.28	%
	Oxygen (by diff)	7.99	%	7.07	%

Appendix III

The results from the Rietveld quantitative analysis and the refined spectra with the different phases for the Southpit coal-West, East and Middle.

Whole Pattern Fitting and Rietveld Refinement

FILE: [Z01649.RAW] SOUTH PIT COAL-WEST

SCAN: 5.0/99.98/0.06/5(sec), Cu, I(max)=1909, 07/21/04 04:44p

PROC: [WPF Control File]

☒ K-alpha2 Peak Present

☒ LS Weighting in $1/\sqrt{I}$

☒ LS Weighting in $\sin(\theta)$

☒ Apply Anomalous Scattering

[Diffractometer LP] Two-Theta Range of Fit = 5.0 - 99.7(deg)

☒ Specimen Displacement - $\cos(\theta) = -0.11637(0.003622)$

☐ Monochromator Correction for LP Factor = 1.0

☐ K-alpha2/K-alpha1 Intensity Ratio = 0.5

Profile Shape Function for All Phases: Pearson-VII, Polynomial(6), Lambda=1.54059Å (Cu/K-alpha1)

Phase ID (5)	Space Group	a	b	c	Alpha	Beta	Gamma
Quartz - SiO ₂	P3 ₂ 21 (154)	4.91452	4.91452	5.40611	90.000	90.000	120.000
Calcite - CaCO ₃	R3c (167)	4.98596	4.98596	16.99629	90.000	90.000	120.000
Pyrite - FeS ₂	Pa3 (205)	5.41768	5.41768	5.41768	90.000	90.000	90.000
Kaolinite 1A - Al ₂ (Si ₂ O ₅)(OH) ₄	C1 (1)	5.16095	9.02539	7.38307	92.235	104.699	89.078
Illite-2M2 - KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	C2/c (15)	9.02968	5.16595	20.38434	90.000	101.701	90.000

Phase ID (5)	From	I/Ic	Wt%	#L	TF
Quartz - SiO ₂	PDF#00-046-1045	3.41(5%)	24.6 (1.5)	34	0.000
Calcite - CaCO ₃	PDF#00-005-0586	2.0(5%)	5.3 (0.4)	36	0.000
Pyrite - FeS ₂	PDF#00-042-1340	1.6(5%)	5.2 (0.4)	21	0.000
Kaolinite 1A - Al ₂ (Si ₂ O ₅)(OH) ₄	FIZ#66571	1.02(0%)	19.0 (1.1)	610	0.500
Illite-2M2 - KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	PDF#00-043-0685	0.36(5%)	46.0 (3.5)	37	0.000

NOTE: Fitting Halted at Iteration 28(4): R=8.81% (E=9.29%, R/E=0.95, P=50, EPS=0.5)

Whole Pattern Fitting and Rietveld Refinement

FILE: [Z01652.RAW] SOUTHPIT COAL EAST

SCAN: 5.0/99.98/0.06/5(sec), Cu, I(max)=2360, 07/22/04 04:58p

PROC: [WPF Control File]

- ☒ K-alpha2 Peak Present [Diffractometer LP] Two-Theta Range of Fit = 5.0 - 99.7(deg)
☒ LS Weighting in 1 / Sqr(I) ☒ Specimen Displacement - Cos(Theta) = -0.141035(0.003352)
☒ LS Weighting in Sin(Theta) ☐ Monochromator Correction for LP Factor = 1.0
☒ Apply Anomalous Scattering ☐ K-alpha2/K-alpha1 Intensity Ratio = 0.5

Profile Shape Function for All Phases: Pearson-VII, Polynomial(6), Lambda=1.54059Å (Cu/K-alpha1)

Phase ID (4)	Space Group	a	b	c	Alpha	Beta	Gamma
Quartz - SiO ₂	P3 ₂ 21 (154)	4.91475	4.91475	5.40620	90.000	90.000	120.000
Pyrite - FeS ₂	Pa3 (205)	5.41825	5.41825	5.41825	90.000	90.000	90.000
Kaolinite 1A - Al ₂ (Si ₂ O ₅)(O...	C1 (1)	5.16459	9.01319	7.39300	92.413	104.941	89.059
Illite-2M2 - KAl ₂ (Si ₃ Al)O ₁₀ ...	C2/c (15)	9.06454	5.17057	20.40375	90.000	101.928	90.000

Phase ID (4)	From	I/Ic	Wt%	#L	TF
Quartz - SiO ₂	PDF#00-046-1045	3.41(5%)	30.7 (1.9)	34	0.000
Pyrite - FeS ₂	PDF#00-042-1340	1.6(5%)	3.6 (0.3)	21	0.000
Kaolinite 1A - Al ₂ (Si ₂ O ₅)(OH) ₄	FIZ#66571	1.02(0%)	19.4 (1.1)	612	0.500
Illite-2M2 - KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	PDF#00-043-0685	0.36(5%)	46.3 (3.6)	37	0.000

NOTE: Fitting Halted at Iteration 30(4): R=9.53% (E=9.05%, R/E=1.05, P=44, EPS=0.5)

Whole Pattern Fitting and Rietveld Refinement

FILE: [Z01653.RAW] SOUTH PIT COAL MIDDLE

SCAN: 5.0/99.98/0.06/5(sec), Cu, I(max)=2455, 07/23/04 02:01p

PROC: [WPF Control File]

- ☒ K-alpha2 Peak Present
☒ LS Weighting in $1/\sqrt{I}$
☒ LS Weighting in $\sin(\theta)$
☒ Apply Anomalous Scattering
- [Diffractometer LP] Two-Theta Range of Fit = 5.0 - 99.7(deg)
☒ Specimen Displacement - $\cos(\theta) = -0.180101(0.003457)$
☐ Monochromator Correction for LP Factor = 1.0
☐ K-alpha2/K-alpha1 Intensity Ratio = 0.5

Profile Shape Function for All Phases: Pearson-VII, Polynomial(6), Lambda=1.54059Å (Cu/K-alpha1)

Phase ID (5)	Space Group	a	b	c	Alpha	Beta	Gamma
Quartz - SiO ₂	P3 ₂ 21 (154)	4.91357	4.91357	5.40522	90.000	90.000	120.000
Calcite - CaCO ₃	R3c (167)	4.98269	4.98269	17.04073	90.000	90.000	120.000
Pyrite - FeS ₂	Pa3 (205)	5.41633	5.41633	5.41633	90.000	90.000	90.000
Kaolinite 1A - Al ₂ (Si ₂ O ₅)(O...	C1 (1)	5.17098	8.99836	7.39316	92.239	104.992	89.058
Illite-2M2 - KAl ₂ (Si ₃ Al)O ₁₀ ...	C2/c (15)	9.05850	5.16781	20.36905	90.000	101.898	90.000

Phase ID (5)	From	I/Ic	Wt%	#L	TF
Quartz - SiO ₂	PDF#00-046-1045	3.41(5%)	30.7 (1.9)	34	0.000
Calcite - CaCO ₃	PDF#00-005-0586	2.0(5%)	3.7 (0.4)	36	0.000
Pyrite - FeS ₂	PDF#00-042-1340	1.6(5%)	5.8 (0.4)	21	0.000
Kaolinite 1A - Al ₂ (Si ₂ O ₅)(OH) ₄	FIZ#66571	1.03(0%)	20.0 (1.1)	614	0.500
Illite-2M2 - KAl ₂ (Si ₃ Al)O ₁₀ (OH) ₂	PDF#00-043-0685	0.36(5%)	39.8 (3.2)	37	0.000

NOTE: Fitting Halted at Iteration 32(4): R=9.82% (E=9.23%, R/E=1.06, P=48, EPS=0.5)