

**Study on the Effect of Coal Drying in Adsorbing CO₂ at Different Temperature and
pH**

by

Suhana bte Muhamad

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

JANUARY 2005

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CERTIFICATION OF APPROVAL

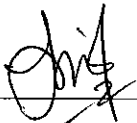
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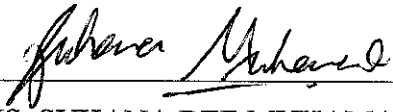
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January 2005

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



MS. SUHANA BTE MUHAMAD

ABSTRACT

CO₂ is the primary green house gas representing roughly 83% of the anthropogenic effect. One of the options to mitigate the rising atmospheric concentration of CO₂ is through CO₂ geologic sequestration in coal seams process. Part of understanding the sequestration is to study what is the effect on the rate of CO₂ adsorption at different temperature and pH in a coal mine environment. The objectives of this study are to investigate CO₂ gas adsorption patterns on local coal sample at different temperature, pH and particle sizes. It is also to determine the basic properties of the local coal sample and determine how the characteristic of the coal sample affects the adsorption rate of CO₂ gas. In the characterization of the coal sample process, there were a number of parameters which was studied and tested. They were the moisture content, the ash content, carbon content and mineral content of the coal sample. For the study on the effect of varying parameters on the CO₂ adsorption on coal seams, the CO₂ adsorption behavior was investigated using a manometric apparatus. The experimental set-up will be used in the investigation of the effects of temperature (24.6^oC, 30^oC, 40^oC and 55^oC) pH (acidic of pH 0.51, near neutral of pH 5.97 and alkali of pH 12.40), and particle size (1000 μ m and 2000 μ m) of the CO₂ adsorption rate on the local coal sample. The moisture content of the coal sample was found to be 37.4%. The ash content analysis gave a percentage ash of 11.02%. The elemental composition analysis gave an elemental carbon content of 56% to 60%. The mineral matter in the coal sample was found to be 12.09%. The chemical elements analysis indicated silica as having the highest amount in the coal sample. The experiments conducted for the study of the CO₂ adsorption in coal seams showed that smaller particle size 1000 μ m had a higher adsorption rate per mass of coal sample as compared to the 2000 μ m sample. The effect of increasing the temperature is to decrease the equilibrium adsorption capacity of the coal samples. It can be observed that the untreated coal sample has the highest extent of adsorption capacity followed by the acidic, alkali and neutral conditions. The coal samples were found to be of lignite type. From literature review, coals of lignite type were found to exhibit the most sorption tendency towards CO₂ as compared to coals of other ranks.

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CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Carbon dioxide (CO₂), which makes up for the majority of the green house gas, was seen to have increased in its concentration in the atmosphere over the years. Our main concern here is the global warming effect which will cause worldwide problems such as ozone reduction and desertification.

In our efforts to control the CO₂ concentration rise, researches have been conducted in many areas. Among them are the sequestrations of CO₂. This generally means taking control over the concentration of CO₂ in the atmosphere. Basically there are a few types of sequestration. They are ocean sequestration, geologic sequestration and terrestrial sequestration. Ocean sequestration is where CO₂ are stored in oceans through direct injection or fertilization. Geologic sequestration is carried out by using natural pore spaces in geologic formations which serve as reservoirs for long term carbon dioxide storage while the third type of sequestration, terrestrial sequestration, is where a large amount of carbon is stored in soils and vegetations, which are our natural carbon sinks. Among these three types of sequestration, geologic sequestration is thought to have the largest potential for near-term application.

Geologic sequestration of CO₂ has also been recognized as an environmentally attractive method to reduce the amount greenhouse gas emissions. Of the geologic options, sequestering CO₂ in coal seams has several advantages. Coal, which is formed through the physical and chemical alteration of peat (coalification) by processes involving bacterial decay, compaction, heat and time, is an agglomeration of many different complex hydrocarbon compounds. Composed of carbon, hydrogen, oxygen, nitrogen, sulfur and other elements, coal can be divided in four major ranks, anthracite coal, bituminous coal, sub-bituminous coal and lignite coal. Coal seams, which are actually the

cracks and fractures on the surface of coal, contain natural gas hydrocarbon compound, formed as a by-product of the coal formation process. These gases, for example methane gases, are also known as coal seam gas (CSG). The basic idea of CO₂ sequestration in coal seams utilizes the basic idea of replacing these coal seam gases with CO₂ gases in the atmosphere.

Among the advantages of CO₂ sequestration in coal seams are that CO₂ injection can enhance methane production from coal beds, coal can trap CO₂ for long periods of time, and potential major coal basins that contain ideal beds for sequestration are near many emitting sources of CO₂. All these compensations contribute to the factor why coal seams option of sequestering CO₂ gas is so appealing.

1.2 PROBLEM STATEMENT

1.2.1 Problem Identification

CO₂ is the primary green house gas representing roughly 83% of the anthropogenic effect. One of the options to mitigate the rising atmospheric concentration of CO₂ is through CO₂ geologic sequestration in coal seams process. In the research of performing geologic sequestration in unminable coal mine, part of understanding the sequestration is to study what is the effect on the rate of CO₂ adsorption at different temperature and pH in a coal mine environment. The main purpose of this research is to study the adsorption patterns of CO₂ gas in coal seams in an environment created in the laboratory that best represent the environment in a coal mine where the actual sequestration will take place. The main two parameters that will be investigated are on the variation of temperature and pH. It is also crucial that the characteristics of the coal are studied upon since the rate of adsorption of CO₂ will differ for each different type of coal.

1.2.2 Significant of Project

The sequestration of the carbon dioxide gas (CO₂) in coal seams is seen as a possible way to mitigate the rising atmospheric concentrations of CO₂. Technologies that have been developed for enhanced oil recovery and enhanced coal bed methane recovery could be

applied to the long term disposal of CO₂. In order to determine which coal seams would be good to act as the disposal sites and under what environmental conditions the sequestered CO₂ would remain stable, a better understanding is needed of the chemistry of the coal-CO₂ system.

This research will study the effects of temperature and pH variation on the adsorption rate of CO₂ gas in coal seams which will provide us crucial information of the optimum environment needed for effective adsorption process of CO₂ to occur in coal mines.

1.3 OBJECTIVES AND SCOPE OF STUDY

1.3.1 Objectives

The objectives of this study are:

1. To investigate CO₂ gas adsorption patterns on local coal sample at different temperature.
2. To investigate CO₂ gas adsorption patterns on local coal sample at different pH.
3. To investigate CO₂ gas adsorption patterns on local coal of different particle sizes.
4. To determine the basic properties of the local coal sample and determine how the characteristics of the coal sample affects the adsorption rate of CO₂ gas.

1.3.2 Scope of Study

The scope of study, as outlined by the objectives above, includes investigating the CO₂ gas adsorption patterns on local coal under temperature variation. The temperatures tested were at 24.6⁰C, 30⁰C, 40⁰C and 55⁰C.

For the investigation of the CO₂ gas adsorption patterns on local coal at different pH, conditions of acidic, near neutral and alkaline with the pH values of 0.51, 5.97 and 12.40 were created for the experiment. This experiment monitors the trend of the adsorption rate of CO₂ in the local coal sample under different pH conditions.

The effects which the coal particle sizes have on the adsorption rate of CO₂ gas were studied upon. Two sizes of coal particles were experimented on (1000µm and 2000µm in diameter).

The general properties of the local coal sample were also studied upon for the purpose of identifying and predicting the performance of CO₂ adsorption in it. The properties investigated were the moisture content, ash content and carbon content.

Similarly, the chemical element analysis, which gives us the approximate amount of chemical content of the coal sample, can then be compared with other coal samples' chemical elemental analysis obtained from literature and give us a clearer understanding of how the adsorption rate is affected by this factor. The chemical elements analysis was conducted using the Atomic Absorption Spectrometer (AAS).

1.3.3 The Relevancy of Project

The extent to which coal can adsorb CO₂ is affected by a number of factors. The nature of the coal will determine the maximum adsorption capacity under a given set of conditions, but the sequestration environment will determine the extent to which that ultimate capacity will be realized. The effects of both physical and chemical changes need to be understood. Parameters such as temperature, pressure and pH is expected to have a moderate to large influence, therefore creating the need for it to be studied upon (K. Schroeder et al).

The investigations on the variation of temperature and pH on the adsorption rate of CO₂ on the coal sample will enable us to predict the optimum temperature and pH conditions for the best adsorption rate of CO₂ gas in the geologic sequestration process to occur. Once the optimum conditions are determined, efforts can be made to identify the unminable coal mines whose conditions fit the identified optimum conditions. This location identification is a crucial first step in ensuring the success of the sequestration process.

In the absence of external influences, underground temperatures tend to be constant over time but increases with depth. The adsorption of CO₂ is exothermic and will provide a heat source, at least during the active pumping phase of sequestration. Thus, it is important to know how temperature will affect the CO₂ adsorption onto coal and whether the magnitude of this effect is universal for all coals or is rank or maceral dependent (K. Schroeder et al). The effects of temperature on the adsorption rate on the different types of coals can be compared through information obtained through literature. From here, we can compare the local coal sample with those from around the world and establish a prediction of the performance of the local sequestration process, should the project be implemented here in Malaysia.

Even if initially dry, coal seams will become wet as a result of drilling operations, fracturing of the coal bed and over lying strata, and the deposition of a combustion gas which may contain residual water of combustion. Thus, an aqueous phase will be present and will vary in composition according to its source and the nature of the coal bed and the surrounding material with which it is in contact. In natural systems, pH is often an important parameter and will change during sequestration. Little is known about the potential effect of a pH change on the ability of the organic matrix to adsorb CO₂. It is well recognized that adsorption of CO₂ on solid surfaces is affected by the pH of the surrounding media (K. Schroeder et al). The extent to which pH changes will affect the CO₂ adsorption capacity of coals has not been investigated thoroughly, therefore need to be established to allow us to predict and take the necessary steps in ensuring the smooth operation of CO₂ sequestration process.

Depending on the capture technology, the CO₂ stream may be as nearly pure as the CO₂ a raw combustion gas, or something in between. In addition, gases such as hydrogen, methane, ethane and higher hydrocarbons may be present in the coal seam and act to inhibit or enhance the CO₂ sequestration. These gases may displace CO₂ and thus limit the durability of the sequestration (K. Schroeder et al). Therefore, it is imperative that the preferential sorption phenomena in coal seams between CO₂ and CH₄ gas are investigated. The CH₄ gas is chosen here due to the fact that it makes up for the majority

of the gases underground and thus established itself as the main opponent of the CO₂ for the adsorption process in coal seams.

Coal contains a wide variety of organic and mineral phases in a complex, porous, 3-dimensional network which varies from one coal deposit to another and from one location to another within the same seam. The organic portion of the coal is thought to capture CO₂ via surface adsorption, pore filling and solid solution. Less recognized is the possibility that the mineral phases present in the coal may assist via mineral carbonate formation. Thus, the nature of the coal seam itself is an important variable to be considered (K. Schroeder et al). This is where the chemical elements analysis comes into the picture. By analyzing the chemical elements of the local coal sample, a general definition of the predicted performance of the CO₂ sequestration in the local coal seams can then be established.

Knowledge of the extent to which coals can adsorb CO₂ under a variety of conditions is necessary to evaluate the long-term storage capacity of candidate seams. The nature of the coal will determine its maximum adsorption capacity, but the dynamic nature of the sequestration environment will determine the extent to which that capacity can be realized. In order to evaluate the long-term storage capacity of a coal seam, possible changes in the sequestration environment need to be anticipated and their effect understood (K. Schroeder et al). The experiments will allow us to study the CO₂ adsorption rate under many possible environments scenarios in a coal mine. The data obtained from the experiments will enable us to have a better analysis and understanding of the CO₂ sequestration process which will, in time, pave the way towards actually implementing such project in Malaysia.

CHAPTER 2

LITERATURE REVIEW AND THEORY

2.1 COAL PROPERTIES

Coal is a heterogenous sedimentary rock, with physical and chemical properties determined by biochemical and geochemical transformation of vegetable matter. The extent of this transformation, known as coalification, is given by the rank of the coal, which is determined on the basis of a chemical (proximate) analysis. The proximate analysis involves the determination of the weight percent of moisture, volatile matter, fixed carbon and ash in the coal under prescribed heating. Coal ranking is a measure of the degree to which the original vegetable matter approaches the structure of pure carbon conditions (M.E.272 Standford University). Rank is a classification of coal beds that indicates the degree of metamorphism, or progressive alteration, from lignite to anthracite (R. Stanton et al).

Anthracite coal is of the highest metamorphic rank. It is also known as “hard” coal and has a brilliant luster. It can be rubbed without leaving a “familiar coal dust” mark on the finger and can even be polished for use as jewelry. Anthracite coal burns slowly with pale blue flame and may be used primarily as a domestic fuel. Bituminous coal burns with a smoky flame and may also contain 15-20% w/w volatile matter. It is the most abundant variety of coal, weathers only slightly, and can be kept in open piles with very little danger of spontaneous combustion. Sub-bituminous coal is not as high on the metamorphic scale as bituminous coal and has often been called “black lignite”. Lignite is the coal that is lowest on the metamorphic scale. It may vary in color from brown-black and is often considered to be intermediate between peat and the sub-bituminous coals. Lignite is often distinguished from the sub-bituminous coals as having lower carbon content and a higher moisture content. Lignite may dry out and crumble in air and is certainly liable to spontaneous combustion (Speight, 1994, p.5).

Table 2.1: Analyses in the Coalification Series

| Material | Wood % | Peat % | Lignite % | Sub- Bituminous Coal % | Bituminous Coal % | Anthracite % |
|------------------------------------|-------------------|-------------------|----------------------|---|----------------------------------|-------------------------|
| Moisture (material as found) | 30-60 | 90+ | 20-40 | 10-20 | 13-1 | 2-3.5 |
| Moisture (air- dried material) | 10-15 | 20-25 | 15-25 | 10-20 | 13-1 | 2-3.5 |
| Dry, ash-free material: | | | | | | |
| Carbon | 50 | 55-65 | 65-73 | 73-78 | 78-92 | 92-96 |
| Hydrogen | 6.0 | 5.5 | 4.5 | 6.0 | 5.3 | 2.5 |
| Oxygen | 43 | 32 | 21 | 16 | 8 | 4 |

Table is obtained from Combustion and Gasification of Coal, A Williams; M. Pourkashanian; J. M Jones; N. Skorupska; pg.28.

As coal rank increases from lignite to anthracite, the density of the coal initially decreases from lignite to high volatile bituminous coal rank as a result of expulsion of water and compaction and the formation of micropores. In low rank coals, which are less than 75 percent C, on a dry, ash-free (daf) basis (lignite and sub-bituminous ranks), surface area has been interpreted as primarily contained in macropores > 20 nm (R. Stanton et al).

In contrast, density of the high volatile bituminous to anthracite coals increases as a result of coalification processes that drive off hydrogen and oxygen. Pores in these higher rank coals are primarily micropores (< 2 nm) and to a lesser extent transitional pores (2-20nm) (R. Stanton et al).

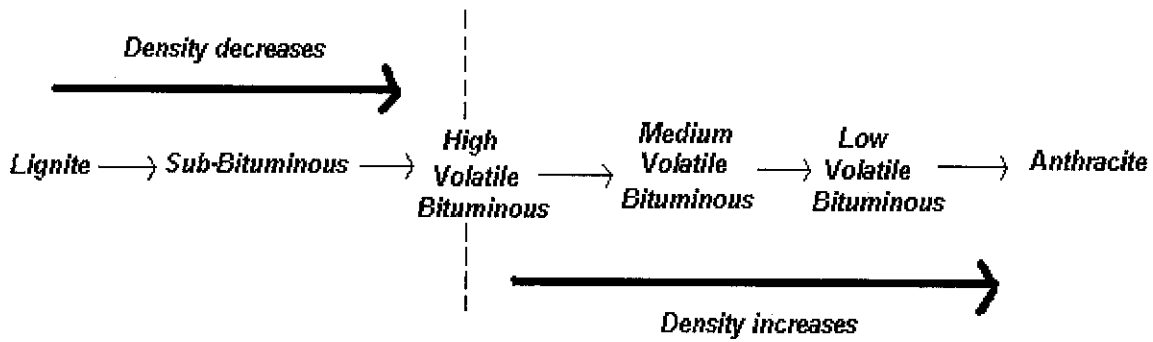


Figure 2.1: Density Trend in Coal Ranks

Because the adsorption capacity is both a function of the amount and reactivity of surface area contained in pores and possibly fractures, understanding the relationships of adsorption of CO₂ and coal rank as well as with the coal composition is of crucial importance. Rank is known to have an effect on the amount of carbon dioxide that can be adsorbed into the coal porosity (R. Stanton et al).

Structurally, coal can be viewed as being composed of water, minerals and organic components (macerals). Organic material dominates, typically representing 85 – 95% (wt/wt) of a dry coal. These organic materials occur in various different petrographic types, called “maceral” which reflect the nature of the precursor plant material. Various inorganic materials comprise 5 – 15% of the coal. A third structural element, and perhaps the most distinctive feature when compared to other solid fossil fuel sources like petroleum and oil shale, is an extensive network of pores. These pores give high surface area (>100 m²/g for bituminous and sub-bituminous coals and lignites) and an appreciable volume of pore space, allowing access to a significant fraction of the organic material (Levine et al, 1981).

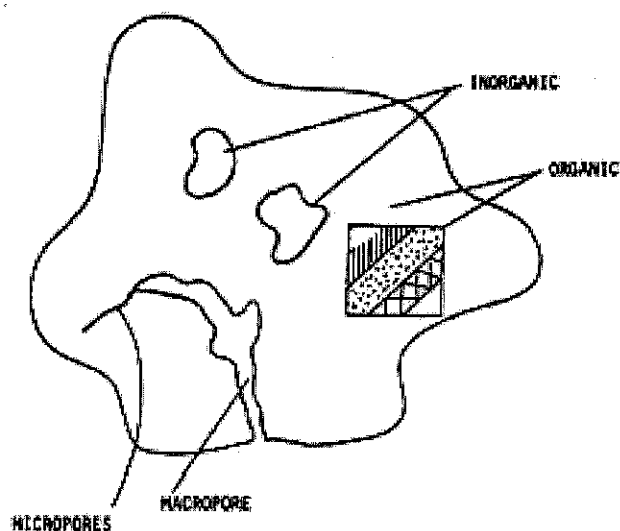


Figure 2.2: Diagram of the major constituents in coal: organic material, fragments of plant debris (macerals), inorganic inclusions, and an extensive pore network.

Macerals are the most combustible components of coal and can vary in chemical composition both among maceral varieties within a single coal bed and among coal beds. The general groups of macerals are vitrinite, liptinite and inertinite. Macerals originate from partially decomposed plant parts that are altered through the coalification process. Their dominant chemical composition is primarily a mixture of carbon, hydrogen, oxygen, nitrogen and sulfur. Of the major maceral groups, liptinite is richer in hydrogen while inertinite is richer in carbon than vitrinite (R. Stanton et al).

As a result of differing peat-forming conditions and plant assemblages, organic components are transformed into macerals which arrange structurally into lithotypes that, in turn, comprise facies or the major subunits of a coal bed. Adsorption properties of coal beds vary with the composition of the coal. Gases should be adsorbed most by vitrain-rich facies that contain low amounts of minerals. Physical properties of a coal bed can also be of significant factor in the adsorption of CO_2 . The properties include fracture intensity, degree of fracture filling, overburden and seat rock permeability, coal rank, reservoir pressure and the degree of folding and faulting of the coal bed (R. Stanton et al).

The most permeable facies are those rich in fusain layers and the most impermeable layers contain discrete mineral layers, impure coal facies that are rich in minerals, or attrital lithotypes (R. Stanton et al).

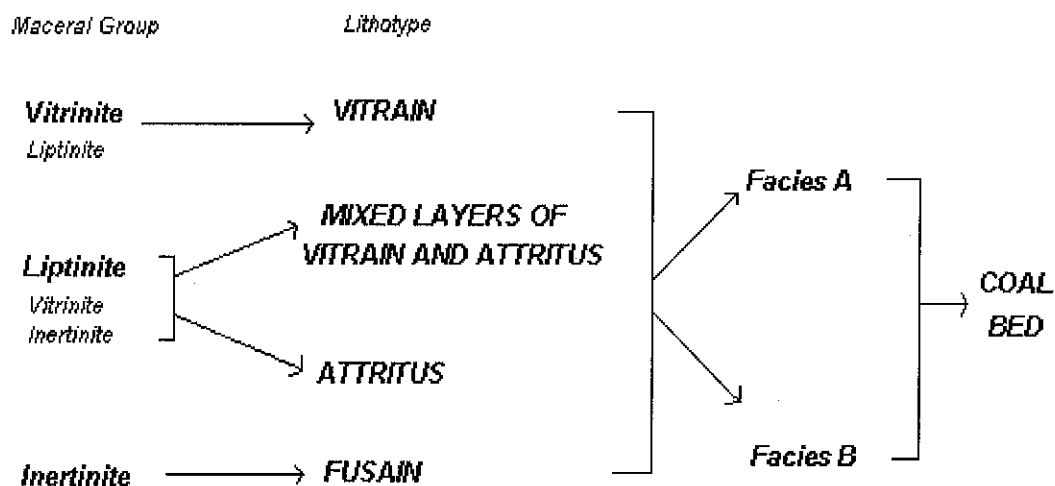


Figure 2.3: Structural relationships among macerals and lithotypes that comprise facies of a coal bed.

The percentage of water in coal (inherent moisture) is used to differentiate coals by rank up to the high volatile bituminous stage. Low rank coals contain more water than higher rank coals. Water content is significant in coals from low to medium rank, ranging from $\approx 40\%$ (wt/wt) for typical lignite to $\approx 14\%$ (wt/wt) for bituminous coal (Levine et al, 1981).

Among the minerals found in coals are Phosphate Pentoxide (P_2O_3), Silica (SiO_2), Ferric Oxide (Fe_2O_3), Alumina (Al_2O_3), Tilania (TiO_2), Lime (CaO), Magnesia (MgO), Sulfur Trioxide (SO_3), Potassium Oxide (K_2O) and Sodium Oxide (Na_2O) (M.E 272 Stanford University). These are among the major minerals that make up the structure of coal. The general representative percentage and the mineral constituents are given below. The major elements that make up for these minerals are also included here.

Table 2.2: Major Inorganic Constituents of Coal Ash

| Constituents | Representative Percentage |
|--------------------------------|---------------------------|
| SiO ₂ | 40 – 90 |
| Al ₂ O ₃ | 20 – 60 |
| Fe ₂ O ₃ | 5 – 25 |
| CaO | 1 – 15 |
| MgO | 0.5 – 4 |
| Na ₂ O | 0.5 – 3 |
| K ₂ O | 0.5 – 3 |
| SO ₃ | 0.5 – 10 |
| P ₂ O ₅ | 0 – 1 |
| TiO ₂ | 0 - 2 |

Table is obtained from The Chemistry and Technology of Coal, Second Edition, James G. Speight.

Table 2.3: Some of the Major Elements in Coals

| Constituent | Range |
|-------------|--------------|
| Aluminum | 0.43 -3.04% |
| Calcium | 0.05 – 2.67% |
| Iron | 0.34 – 4.32% |
| Potassium | 0.02 – 0.43% |
| Magnesium | 0.01 – 0.25% |
| Sodium | 0.00 – 0.20% |
| Silicon | 0.58 – 6.09% |
| Titanium | 0.02 – 0.15% |

Table is obtained from The Chemistry and Technology of Coal, Second Edition, James G. Speight.

A wide variety of pore sizes exists in coal of different ranks, ranging from large ($\geq 300 \text{ \AA}$) macropores to small ($\leq 12 \text{ \AA}$) micropores. Knowledge of the total volume of

such pores, the pore size distribution, and the effective surface area of the organic material is needed to anticipate coal's potential reactivity (Levine et al, 1981).

2.2 EXPERIMENTAL METHODOLOGY

From literature reviews, there were some experimental methodologies found for the purpose of studying the adsorption of CO₂ in coal seams. These methods has been reviewed and modified to suit with the available apparatus in the laboratory for the purpose of the study.

(A. Busch, Y. Gensterblum, B.M. Krooss) on their study of Methane and CO₂ Sorption and Desorption Measurements on Dry Argonne Premium Coals: Pure Components and Mixtures, had utilized the volumetric gas adsorption method. The experimental set-up consisted of a stainless steel reference and sample cell, actuator-driven valves and a high precision pressure transducer. The cells are placed in a thermostated water bath for temperature calibration. The coal samples are kept in a stainless steel sample cell with a calibrated volume. The experiments are carried out by first evacuating both the sample and reference cell, before a certain amount of gas are admitted to the reference volume and calibrated. From the experiments, the pressure reductions readings in the sample cell containing the coal sample are taken. Using an equation of state (EOS), the amount of substance (moles of gas) in the reference cell is computed from the pressure, temperature and volume of the cell. The reduction in the number of moles indicates the amount of CO₂ gas adsorbed in the coal sample.

(K. Schroeder, E. Ozdemir, B.I Morsi) in their study of Sequestration of Carbon Dioxide in Coal Seams had also used the manometric principle in their experimental set-up which consisted of a reference and sample cell of known volume which was placed in a water bath. The sample cell was pressurized from the reference cell. Using the change in pressure in the reference cell and accounting for the gas compressibility, the number of moles of gas transferred from the reference cell was calculated. The number of gas-phase moles in the sample cell after the gas transfer was calculated from the post-transfer

sample-cell pressure in a similar manner. The missing moles of gas were accounted to the adsorption of CO₂ onto the coal.

2.3 EFFECT OF PARAMETERS VARIATION ON CO₂ ADSORPTION

2.3.1 Effect of Temperature

From the experiments conducted under the research of K. Schroeder, E. Ozdemir and B.I Morsi, it was found that increased temperature caused a decrease in the equilibrium adsorption capacity of the coal. The tested temperatures were of 22⁰C, 30⁰C, 40⁰C and 55⁰C.

It was also found that the incremental amount of CO₂ that can be adsorbed by the coal drops off at higher pressures. From a practical stand-point, this meant that a higher pumping cost per pound of CO₂ will be incurred at higher sequestration pressures. In the pressure-temperature region studied (0 – 700 psi and 0 – 55⁰C), the CO₂ capacity did not exceed 1.4mmole CO₂/g coal. This adsorption value correspond to a CO₂ storage density of about 85kg CO₂/m₃ coal.

2.3.2 Effect of pH

(K. Schroeder, E. Ozdemir and B.I Morsi) had also included pH variation effects in their study of CO₂ sequestratio since the pH of an aqueous solution affects the surface of a material it is in contact with.

The major difference observed from the experiments was the lower extent of adsorption for the samples that were treated, irrespective of the treatments. Among the treated samples, it was found that both acid and base treatment resulted to an increase in adsorption capacity compared to the coal treated with only de-ionized water.

2.3.3 Effect of Mineral Content in Coal

From the pH variation experiments conducted by K. Schroeder, E. Ozdemir and B.I Morsi, the acid treated sample was found to be lower in its mineral content due to the removal of acid-soluble minerals during the treatment process. The increased in the adsorption of CO₂ for the acid treated sample was identified to be due to the increased accessible pore volume which was caused by the removal of mineral content from the coal sample. This finding establishes a relationship between the adsorption capabilities of a coal sample with its mineral content where lower mineral content containing coals will be able to adsorb CO₂ better as compared to coals with high mineral content.

CHAPTER 3

PROJECT METHODOLOGY

3.1 COAL CHARACTERIZATION IDENTIFICATION

3.1.1 Experimental Procedure Utilized

The project involves identifying the general nature and type of the coal sample obtained from the coal mines in Sarawak. Since there was no information given regarding the characteristics of the coal, this characterization identification was a crucial step in determining and predicting the effects on the CO₂ adsorption as critical parameters (e.g. temperature, pH) are varied. This is due to the fact that coals of different rank and mineral content will behave differently to the adsorption process. In other words, this coal characterization step will enable us to predict the performance of the CO₂ sequestration if it were to be implemented on our local coals here in Malaysia.

In the characterization process, there were a number of parameters which was studied and tested. They were the moisture content, the ash content, carbon content and mineral content of the coal sample. The procedures for each of these experiments are discussed below.

3.1.1.1 Moisture Content Analysis

The coal sample (passing 250 μ m sieve) was taken and placed in a pre-weighed Petri dish and weighed. The Petri dish containing the coal sample was then placed for an hour inside an oven at a temperature of 110⁰C. The sample was then weighed again to determine the weight loss from the heating process. The loss of weight from the coal sample was taken as the moisture content of the coal sample.

3.1.1.2 Ash Content Analysis

The coal sample was grinded to pass a 150 μ m sieve. With an open 50mL quartz/high silica crucible used as the container, approximately 6g of this grinded coal sample was placed in a cold muffle furnace and heated gradually till the temperature reaches 300⁰C in

an hour. The heating process was continued till the temperature reached 500⁰C in the second hour. Ashing was continued for another 2 hours at 500⁰C. The sample was stirred once each hour. At the end of the 2 hours, the sample was cooled and reweighed, before being grinded and reignited at 500⁰C for an additional hour. The resulting sample was cooled and reweighed again to calculate the percentage ash.

3.1.1.3 Elemental Composition Analysis (Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen Content Analysis)

The CHNS-O analysis was performed on the coal sample using the CHNS-O Equipment. 5 samples were tested which consisted of the coal sample with the particle size of <150 μ m. The coal sample of <150 μ m was oven dried first to remove the moisture from the sample prior to the experiment.

3.1.1.4 Chemical Element Analysis

The coal sample was analyzed for its chemical element content. From literature review, it was known that coals will generally contain some major minerals which are Phosphate Pentoxide (P₂O₃), Silica (SiO₂), Ferric Oxide (Fe₂O₃), Alumina (Al₂O₃), Tilania (TiO₂), Lime (CaO), Magnesia (MgO), Sulfur Trioxide (SO₃), Potassium Oxide (K₂O) and Sodium Oxide (Na₂O). Through the use of the Atomic Absorption Spectrometer (AAS), these chemical elements were detected.

The usage of the AAS required the coal sample to be in liquid form. Thus, the coal sample had to be liquefied first using a method obtained from the American Standard of Testing Materials (ASTM) 2000. The preparation of reagents needed was done prior to the dissolution process. The following reagents were prepared as follows:

- a) Aqua Regia Solution – One part of concentrated nitric acid (HNO₃) was mixed with three parts of concentrated hydrochloric acid (HCl) and one part water.
- b) Boric Acid Solution, Saturated – 60g of boric acid (H₃BO₃) was dissolved in 1L of de-ionized water.

- c) Stock Solutions, Standard – Standard stock solutions were prepared from high-purity metals, oxides, or salts.
- d) Hydrofluoric Acid – Concentrated hydrofluoric acid (HF).

The dissolution process was carried out by placing approximately 0.2 g of ashed coal sample in a 25mL sample containers. 3mL of Aqua Regia solution and 5mL of HF was added to this. With the screw caps tightened, the samples were then heated at a temperature of 130⁰C for at least 2 hours after which the resultant solution was then transferred to 100mL cylindrical flasks and 50mL of saturated H₃BO₃ solution was added. The solution was cooled to room temperature and their volume was adjusted to 100mL by the addition of de-ionized water. Blanks were also prepared in a similar manner. This final solution obtained was then tested against standard solutions prepared for the identified metal components using the AAS.

3.2 CO₂ ADSORPTION EXPERIMENTS

3.2.1 Experimental Set-up

For the study on the effect of varying parameters on the CO₂ adsorption on coal seams, the following experimental apparatus was constructed.

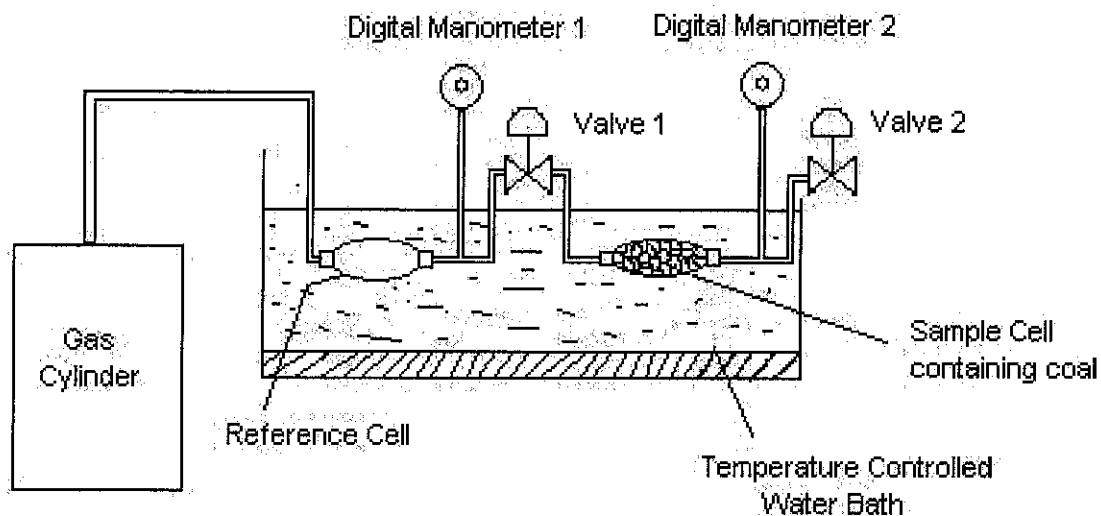


Figure 3.1: Experimental Set-up of Equipment.

The CO₂ adsorption behavior was investigated using an almost similar manometric technique as stated in the literature review. Basically, 2 gas bombs are connected together by plastic tubes with a ball valve. The ball valve functions to control the gas flow from the first reference bomb to the second bomb (containing coal sample). The reference bomb here was used primarily for the purpose of controlling the pressure in the system. At the other end of the sample bomb, another ball valve is placed. This valve functions to either prevent the gas from escaping to the atmosphere and to provide an outlet connection of the experimental apparatus. At the end of each bomb, a digital manometer is placed for the purpose of pressure measurement and monitoring. The experimental set-up is placed in a temperature controlled water bath.

The above experimental set-up will be used in the investigation of the effects of temperature, pH and particle size of the CO₂ adsorption rate on the local coal sample.

3.2.2 Particle Size Variation Experiment

For the particle size variation, the coal sample was grinded and sieved into different particle sizes ranging from < 150 μ m to 2000 μ m. The particle size effect on the adsorption rate was conducted using the particle sizes of 1000 μ m and 2000 μ m at a temperature of 40⁰C. The smaller sized particles (<150 μ m) was utilized for other experimental purposes involving the determination of the sample coal characteristics.

3.2.3 Temperature Variation Experiment

For the temperature variation, the temperatures of 24.6 ⁰C, 30 ⁰C, 40 ⁰C and 55 ⁰C were tested. The temperatures were set so as to give the best representation of the reservoir conditions. The coal sample used here was of the 1000 μ m.

3.2.4 pH Variation Experiment

For the pH variation, the effect of the coal surface pH was investigated by pre-soaking the coal using aqueous slurries at pH values of approximately 0.51, neutral, 12.54 and untreated (acidic, neutral, alkali and untreated conditions respectively). The coals were then filtered and dried overnight in an oven at 60⁰C before being experimented on. The

experiment was conducted at temperature of 40⁰C, so as to simulate the reservoir conditions. The coal sample used here was of the 1000 μ m.

It should be noted that the coal samples were evacuated in an oven at 80⁰C overnight prior and after conducting the experiments.

3.2.5 Experimental Procedure

The coal samples to be tested using the experimental set-up were first treated by evacuating them in an oven overnight at 80⁰C. This is done so as to remove any entrapped gases in the coal seams and to allow the maximum adsorption of CO₂ to occur.

The coal samples were placed in a metal bomb container (approximately more than $\frac{3}{4}$ full) and after tightening the bomb, it was then connected to the rest of the apparatus. Note here that the water bath was set to the desired water temperature prior to the loading of the coal containing sample cell. Extra care was taken here to ensure that the connections were leakage proof. Once the experimental set-up was completed, nitrogen gas (N₂) was flowed through the system. This was done for approximately 3 minutes to purge out any gases in the system prior to the adsorption process.

Once purged, CO₂ gas was then flowed through the system. The flow rate of CO₂ and the opening of the outlet valve (Valve 2) were adjusted so as to maintain a stable pressure inside the system. The stable pressure was achieved once valve 2 can be closed completely without any connections in the system popping open. This stable pressure was usually achieved approximately at 60kPa.

With the stable pressure inside the system, the temperature calibration of the CO₂ gas was then done by closing off the connecting valve between the reference and sample cell (Valve 1). This closure allows the containment of CO₂ gas inside the sample cell system and also calibrates its temperature.

The pressure in the sample cell system was then observed. Once it has reached approximately 17kPa, the pressure readings were taken once every minute till the pressure reaches 0kPa.

Once the pressure readings were taken, the sample cell was then disconnected from the apparatus, and the weighing of the coal sample was done. The coal sample were then placed in an oven and evacuated overnight at 80°C.

The pressure readings taken were corrected to 17kPa for the purpose of synchronizing the readings. The pressure reductions for each of the readings were then calculated and divided by the mass of the coal sample. This gave the pressure reduction of CO₂ per mass of coal sample, which was then plotted against time for the purpose of studying the trend of the adsorption process.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 COAL CHARACTERIZATION IDENTIFICATION - RESULTS

The experiments conducted for the purpose of the sample coal characterization were the moisture, ash, carbon, and mineral content analysis. These experiments were conducted so as to determine the type and characteristics of local coal sample. This determination is of crucial importance since coals of different rank, for example, has different CO₂ adsorption trends.

4.1.1 Moisture Content Analysis

The following results were obtained from the moisture content analysis conducted on the local coal sample.

Table 4.1: Results from Moisture Content Analysis

| | 1st | 2nd | 3rd | Average |
|---|---|-----------------------|-----------------------|----------------|
| | Reading | Reading | Reading | |
| Weight of Petri Dish - empty (g) | 65.0570 | 65.0575 | 65.0571 | 65.0572 |
| Weight of Petri Dish + Coal Sample (g) | 92.6499 | 92.6490 | 92.6484 | 92.6491 |
| Weight of Petri Dish + Coal Sample after heating (g) | 82.3304 | 82.3381 | 82.3433 | 82.3373 |
| Weight of Water (g) | $92.6491 - 82.3373 = 10.3118$ | | | |
| Percentage of Water (Moisture Content) (%) | $\frac{10.3118}{92.6491 - 65.0572} \times 100\% = 37.4\%$ | | | |

4.1.2 Ash Content Analysis

The following are the results of the ash content analysis of the local coal sample.

Table 4.2: Results from Ash Content Analysis

| | 1 st Reading | 2 nd Reading | 3 rd Reading | Average |
|---|--|----------------------------|----------------------------|---------|
| Weight of high-silica crucible (x_1) (g) | 45.2935 | 45.2933 | 45.2935 | 45.2934 |
| Weight of coal sample (x_2) (g) | 6.0048 | | | |
| Weight of crucible + coal sample after first cooling (x_3) (g) | 45.6451 | 45.6466 | 45.6472 | 45.6463 |
| Weight of crucible + coal sample after second cooling (x_4) (g) | 45.6458 | 45.6463 | 45.6469 | 45.6463 |
| Percentage ash (%) | $= \frac{\left([x_1 + x_2] - \left[\frac{x_3 + x_4}{2} \right] \right)}{(x_1 + x_2)} \times 100\%$ $= \frac{51.2982g - 45.6463g}{51.2982g} \times 100\% = 11.02\%$ | | | |

4.1.3 Elemental Composition Analysis (Carbon, Hydrogen, Nitrogen, Sulfur and Oxygen Content [CHNS-O])

The following are the results from the CHNS-O analysis conducted.

Table 4.3: Results from CHNS-O Analysis

| | Carbon (%) | Hydrogen (%) | Nitrogen (%) | Sulfur (%) | Oxygen (%) |
|-------|---------------|-----------------|-----------------|---------------|---------------|
| Run 1 | 56.31 | 4.071 | 1.900 | 0.364 | 26.335 |

| | | | | | |
|--------------|-------|-------|-------|-------|--------|
| Run 2 | 58.46 | 4.285 | 1.957 | 0.402 | 23.876 |
| Run 3 | 57.74 | 4.330 | 1.922 | 0.379 | 24.609 |
| Run 4 | 56.17 | 3.909 | 1.888 | 0.300 | 26.713 |
| Run 5 | 60.24 | 4.200 | 1.889 | 0.279 | 22.372 |

Note: The oxygen percentage was calculated by subtracting the sum of the other components of ultimate analysis from 100 [% Oxygen = 100 – (%C + %H + %N + %S + %Ash) (ASTM D3176).

4.1.4 Mineral Matter Percentage

Using the results obtained from the ash percentage and the average percentage of sulfur compound from the elemental compound analysis, the percentage of the mineral matter can be calculated as below using the Parr formula. Here, [A] is the ash percentage while [S] is the sulfur percentage taken as the average:

$$\% \text{ Mineral matter} = 1.08A + 0.55S = 1.08 (11.02) + 0.55 (0.3448) = 12.09\%.$$

4.1.5 Chemical Elements Analysis

The following results were obtained from the Atomic Absorption Spectrometer (AAS) for the purpose of detecting the metal content in the coal sample. These metals make up for the minerals in the coal sample. The results obtained from the analysis are shown below.

Table 4.4: Results from the Atomic Absorption Spectrometer (AAS) Analysis

| Metal | Concentration (ppm) | Concentration (%) |
|----------------|----------------------------|--------------------------|
| Calcium (Ca) | 3.14 | 3.14×10^{-4} |
| Sodium (Na) | 2.95 | 2.95×10^{-4} |
| Magnesium (Mg) | 1.31 | 1.31×10^{-4} |
| Potassium (K) | 12.40 | 1.24×10^{-3} |
| Iron (Fe) | 23.94 | 2.394×10^{-3} |
| Silica (Si) | 436.34 | 4.363×10^{-2} |
| Aluminum (Al) | 155.9 | 1.559×10^{-2} |

4.2 COAL CHARACTERIZATION IDENTIFICATION - DISCUSSIONS

The summary of the obtained results from the above analysis are given below.

Table 4.5: Summary of Results from Analysis of Coal Sample

| Analysis | Results |
|------------------------------|---|
| <i>Moisture Content</i> | 37.4 % |
| <i>Ash Content</i> | 11.02 % |
| <i>Mineral Matter</i> | 12.09 % |
| <i>Elemental Composition</i> | Carbon ~ 56 – 60 % Hydrogen ~ 3.9 – 4.3 % Nitrogen ~ 1.89 – 1.95 % Sulfur ~ 0.28 – 0.4 % Oxygen ~ 22.4 – 26.3 % |

4.2.1 Coal Rank

In general sense, coal can be defined as an organic rocklike natural product with its resemblance to rock is due to its physical nature and composition. The kinds of plants from which the coal originated, the kinds of minerals inclusions, and the nature of the maturation conditions that prevailed during the metamorphosis of the plant material gives rise to different coal types. The rank of a coal refers to the degree of metamorphosis. For example, coal that has undergone the most extensive change or metamorphosis has the highest rank (determined from the fixed carbon or heating value). The grade of a coal refers to the amount and kind of inorganic material (mineral matter) within the coal matrix (Speight, J.G).

Coal contains significant proportions of carbon, hydrogen and oxygen with lesser amounts of nitrogen and sulfur. Attempts have been made to classify coal on the basis of elemental composition and one of the early classification systems based on the elemental composition of coal (done by Seyler) was subsequently extended (Francis, 1961). For

coals below the anthracite rank and with an oxygen content less than 15%, it was possible to derive a relationship between carbon content (C, %w/w), hydrogen content (H, %w/w), caloric value (Q, cal/g), and volatile matter (VM, %w/w). However, their applications are limited due to applicability to only specific coal types. Nonetheless, this classification does offer an initial attempt to quantify coal behavior (Francis, 1961).

Coal rank is often equated directly with carbon content, since rank does progress from high-carbon coal to low-carbon coal (or vice-versa). However, other properties of the coal are also taken into consideration in assigning rank. The American Society for Testing and Materials (ASTM, 1991) has evolved a method of coal classification that relies on the fixed carbon content of the coal as well as other physical properties. This table is included in the appendix of the report.

This system of classification indicates the degree of coalification as determined by methods of proximate analysis, with lignite being classed as low-rank coal and anthracite as high-rank coal. Thus, coal rank increases with the amount of fixed carbon (which is the solid residue, other than mineral ash, remaining after all of the volatile matter has been removed under prescribed conditions and calculated by subtracting the percentages of moisture, volatile matter and ash from 100%) but decreases with the amount of moisture and volatile matter. This is why coal rank is often equated to the proportion of elemental carbon. Although it is true that anthracite coal usually contains more carbon than bituminous coal, which in turn contains more carbon than sub-bituminous coal, and so on, the distinctions between the proportions of elemental carbon in various coals are not so well defined as for the fixed carbon, and extreme precaution was advised in attempting to equate coal rank with proportion of elemental carbon (Speight, J.G).

From the results of the experiments conducted, it was found that the local coal sample contained a very high value of total moisture content (37.4%). From literature review, it was generally stated that high values of moisture content in coals indicates a lower ranking coal type, with lignite having a value of approximately 20 - 40%.

The elemental composition analysis gave an approximation range of 56.31% to 60.24% of the elemental carbon content in the coal sample. This, together with the moisture content analysis enabled the determination of the rank of the coal sample. From the literature review done, these results indicate that the coal sample are of lignite type, which is the lowest rank in the coal ranking system. Although precautions were advised in the literature reference by J.G Speight in equating coal rank with proportions of elemental carbon instead of the fixed carbon value, this approximation was seen to be fit since the moisture content of the coal sample were found to very high and the oxygen content of the coal sample falls within the 20% - 30% range, which is the lignite type range. These facts therefore support the conclusion that the coal samples studied were of lignite type.

4.2.2 Mineral Matter

Mineral matter in coal originates from the inorganic constituents of the vegetation that acted as the precursor to the coal and from the mineral matter that was transported to the coal bed from any remote site. Thus, mineral matter in coal has often been classified as inherent or extraneous (Francis, 1961; Stach et al., 1982). Inherent mineral matter is defined as mineral matter that had its origin in the organic constituents of the plants giving rise to the coal bed, whereas extraneous mineral matter is matter that was brought into the coal-forming deposit by mechanical means from outside.

Mineral matters in coals are usually determined indirectly, with the ash analysis forming the basis of the calculation. Ash is the residue derived from the mineral matter during complete incineration of the coal. However, determination and chemical analysis of the ash content gives the average content of the inorganic elements in it. Nevertheless, ash analysis can provide valuable data that, when used with data from other sources, may give a representation of the mineral content of the coal (Speight, J.G). Thus, the Parr formula was utilized to assess the mineral matter in coal. The mineral matter content of coal varies considerably and may even be as high as 35% of the coal by weight.

Through the ash content analysis, it was found that the coal sample had a percentage ash of 11.02%. From the ash content and the average sulfur content obtained from the elemental composition analysis, the percentage of mineral matter in the coal sample was determined and found to be approximately 12.09%.

The evaluation of coal mineral matter was taken further by determining the individual metal constituents of the ash. This was done by utilizing the Atomic Absorption Spectrometer (AAS) in which spectra are obtained for standards and samples aspirated into a flame. The obtained results are shown below. It can be seen here that Silica (Si) exists in the largest amount in the coal sample, followed by Aluminum (Al), Iron (Fe), Potassium (K), Calcium (Ca), Sodium (Na) and finally Magnesium (Mg). However, these elements are present in very small amounts if they were compared to the generally found amounts of elements given in the literature review. Nonetheless, the order of which they exist (quantitatively) follows quite closely the general major inorganic constituents of coal ash obtained from literature review. Here, it can be concluded that the coal sample was found to contain small amount of the tested elements. The calculated mineral matter of 12.09% may consist of other elements, which could explain why the tested elements were found to be small in its quantity.

Table 4.6: Results of Chemical Elements Analysis

| Analysis | Results |
|-------------------------|--|
| <i>Chemical Element</i> | Calcium ~ 3.14ppm Sodium ~ 2.95ppm Magnesium ~ 1.31ppm Potassium ~ 12.40ppm Iron ~ 23.94ppm Silica ~ 436.34ppm Aluminum ~ 155.9ppm |

4.2.3 CO₂ Adsorption in Coals as a Function of Rank and Composition

From literature review, based on a research done by Robert C. Burruss under the USGS research on geologic sequestration, it was found that lower ranking coals have a larger ratio of CO₂/CH₄ adsorption as compared to higher ranking coals. The lower ranking coals have a greater tendency to adsorb CO₂ compared to CH₄. This meant that lower ranking coals are better candidates for the purpose of CO₂ sequestration compared to higher ranking coals. It was also found that increase in the moisture content of the coal increases the CO₂/CH₄ adsorption ratio. This meant that higher moisture containing coal will perform better in adsorbing CO₂. There was no obvious correlation found for the CO₂ adsorption with rank and composition. However, it was observed that the CO₂ adsorption is highest for anthracite coals followed by lignite, bituminous and sub-bituminous.

Discussing the results obtained with the literature review above, it can be concluded that the local coal sample is a very good candidate to be utilized as the medium for CO₂ sequestration. This is based on the fact that the coal was identified as lignite type and has high moisture content which, from the literature review, is the mark of a good coal type to adsorb CO₂.

4.3 CO₂ ADSORPTION EXPERIMENTS

4.3.1 Introduction

The main purpose of conducting the CO₂ adsorption experiments was to investigate how the rate of the adsorption process is affected when certain identified critical parameters which are the particle size, temperature and pH conditions of the studied coal sample are varied.

Generally speaking, adsorption processes is where one or more components of a gas or liquid stream are adsorbed on the surface of a solid adsorbent and a separation is accomplished (Geankoplis, C. J.). It involves transfer and resulting equilibrium distribution of one or more solutes between fluid phase and particles. The portioning of a

single solute between fluid and sorbed phases or the selectivity of a sorbent towards multiple solutes makes it possible to separate solutes from a bulk fluid phase or from one another. Adsorption involves, in general, the accumulation (or depletion) of solute molecules at an interface. The accumulation per unit surface area is small, thus, highly porous solids with very large internal area per unit volume are preferred. Adsorbent surfaces are often physically and/or chemically heterogenous, and bonding energies may vary widely from one site to another.

The adsorption separation is based on three distinct mechanisms; steric, equilibrium and kinetic mechanisms. In the steric separation mechanism, the porous solid has pores having dimension such that it allows small molecules to enter while excluding large molecules from entry. The equilibrium mechanism is based on the solid having different abilities to accommodate different species, that is the stronger adsorbing species is preferentially removed by the solid. The kinetic mechanism is based on the different rates of diffusion of different species into the pore, thus by controlling the time of exposure the faster diffusing species is preferentially removed by the solid (Do, Duong D.).

There are basically two types of adsorption. The first being physisorption, which involves van der Waals forces. This type of adsorption occurs when the intermolecular forces between molecules of a solid and the gas are greater than those between the gas molecules itself. The second type of adsorption is of the chemisorption which occurs through the formation of chemical bonds between the gas and coal.

In our case, the type of adsorption occurring are of the physisorption type. The intermolecular forces between the CO₂ gas (adsorbate) and the coal, which acts as the adsorbent, are stronger as compared to the intermolecular forces between the CO₂ molecules themselves. This promoted the adsorption of the CO₂ into the coal seams and hence created the opportunity for us to study the possibility of utilizing this simple process for the purpose of CO₂ sequestration to mitigate the rising CO₂ concentration in the atmosphere.

4.3.2 Experimental Procedure Justification

The experimental procedure utilized the manometric principles which are often utilized in CO₂ sequestration in coal seams researches all over the world. The main reason behind this common utilization is due to the fact that the study applies the philosophy of the non-ideal gas law to measure the number of molecules adsorbed by the coal sample. This simple principle is shown below.

$$PV = ZnRT \quad [1]$$

Where:

P = Pressure of Sample Cell (kPa)

V = Volume of Sample Cell (m³)

n = Number of Moles of Gas in Sample Cell (moles)

R = Universal Gas Constant (8.314 kJ/kmol.K)

T = Temperature of the Sample Cell (°C)

Z = Compressibility factor for Sample Gas

Rearranging the equation will result in the following:

$$P = \left[\frac{ZRT}{V} \right] n \quad [2]$$

Assuming the $\left[\frac{ZRT}{V} \right]$ factor remains constant, the pressure of the sample cell P , can be observed to be directly proportional to the number of CO₂ gas moles in the sample cell n . Thus, relating to the conducted study, the pressure reduction readings taken during the experiment, when plotted against the time period, were actually directly proportional to the loss in the number of moles of CO₂ gas in the system. This is shown below.

$$\Delta P = \left[\frac{ZRT}{V} \right] \Delta n \quad [3]$$

Hence, the trends observed in the plotted graphs can be taken as representatives of the rate of adsorption of CO₂ gas into the coal sample seams, which is our main focus in the research and thus justifies the method used in the experiments.

4.3.3 Experimental Operating Conditions Justification

The operating conditions of the conducted experiments (particle sizes, temperature and pH conditions) were decided upon based on literature review done on similar researches conducted and also upon the ease and practicality of the experimental set-up.

The temperature and pressure chosen for the experiments were of fundamental importance since both play a crucial part in distinguishing the physical properties of the CO₂ gas. Thus, proper care was taken in choosing the operating temperature and pressure so as to maintain the CO₂ gas in gas phase. This was done by choosing and maintaining both of these parameters below the critical point of CO₂ gas (31⁰C and 1070 psia). Increase in the pressure of the gas at temperatures below the critical point will result in condensation of the gas and cause in an apparent increase in the adsorbed amount of CO₂ gas in the system. This will clearly result in inaccurate data and thus was avoided.

Another factor considered when choosing these parameters are the practicality and feasibility of the operating parameters with the experimental set-up. Since the set-up had to be constructed independently by the author, it could not handle high pressure. The maximum pressure attainable in the system was around 80kPa. Thus, the conducted experiments were conducted below this maximum system pressure.

The choices for temperatures the purpose of studying the variation effects were based upon the decision to simulate the reservoir temperatures as closely as possible. From literature reviews done on the subject of CO₂ sequestration, the temperature was set at the maximum of 55⁰C to simulate the reservoir temperature. This indicates that the temperature is higher in the coal mines. However, there were also some researches which conducted the experiments at lower temperatures of 22⁰C. Thus, the temperatures were chosen to be within these two values with the lowest temperature 24.6⁰C, due to

limitations of the water bath temperature. For the particle size and pH condition variations, the temperature of 40°C and coal particle sizes of 1000µm was utilized for the sole purpose of synchronizing the experiments.

The experiments conducted for the study of the CO₂ adsorption in coal seams consisted of varying the parameters of particle size, temperature and pH of the coal samples. The results of these experiments are discussed below.

4.3.4 Particle Size Variation Experiment

The results for the particle size variation experiments are plotted below.

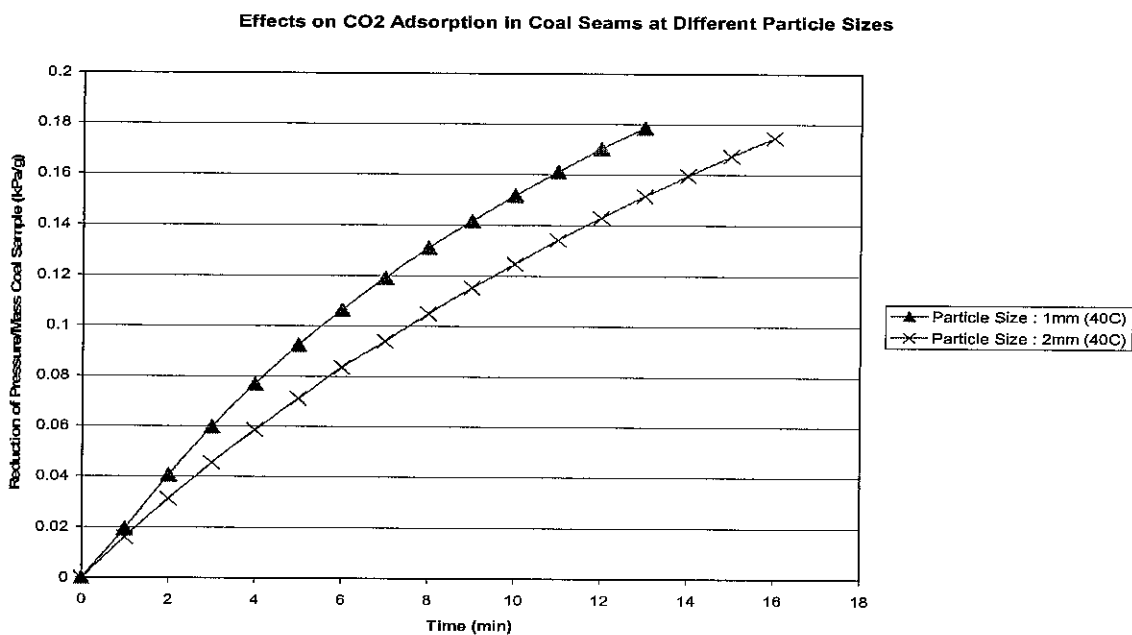


Figure 4.1: Effect on CO₂ Adsorption in Coal Seams at Different Particle Sizes (1000µm and 2000µm) at 17kPa.

The effect of different particle sizes on the CO₂ adsorption in coal seams were investigated using coal samples of two different particle sizes, 1000µm and 2000µm. As shown in the plotted graph in Figure 4.1, the smaller particle size 1000µm had a higher adsorption rate per mass of coal sample as compared to the 2000µm sample.

As in any other subject matter, smaller particles size will result in a larger surface area of the material. In this case, a larger surface area caused the coal seams to be more exposed to the CO₂ gas, thereby enhancing the rate of adsorption. This can be observed by the higher rate of pressure reduction per mass coal sample as plotted.

However, for the purpose of CO₂ sequestration, it should be noted that although smaller particles of a given mass of coal sample will have a greater surface area as compared to larger particles (thus enhancing the rate of adsorption), the coal's huge internal surface area dominates so much that the particle size essentially has no effect on the capacity of the coal to adsorb CO₂. In other words, the particle size of the coal will have not much of a significant impact on the rate of CO₂ adsorption in large scale operations.

Comparing the results obtained from the conducted experiments on the identified lignite coal sample with the data of previously conducted research done on bituminous coal sample, the following graph was obtained. Here, the Indonesian coal is of bituminous type while the local coal sample is of lignite type.

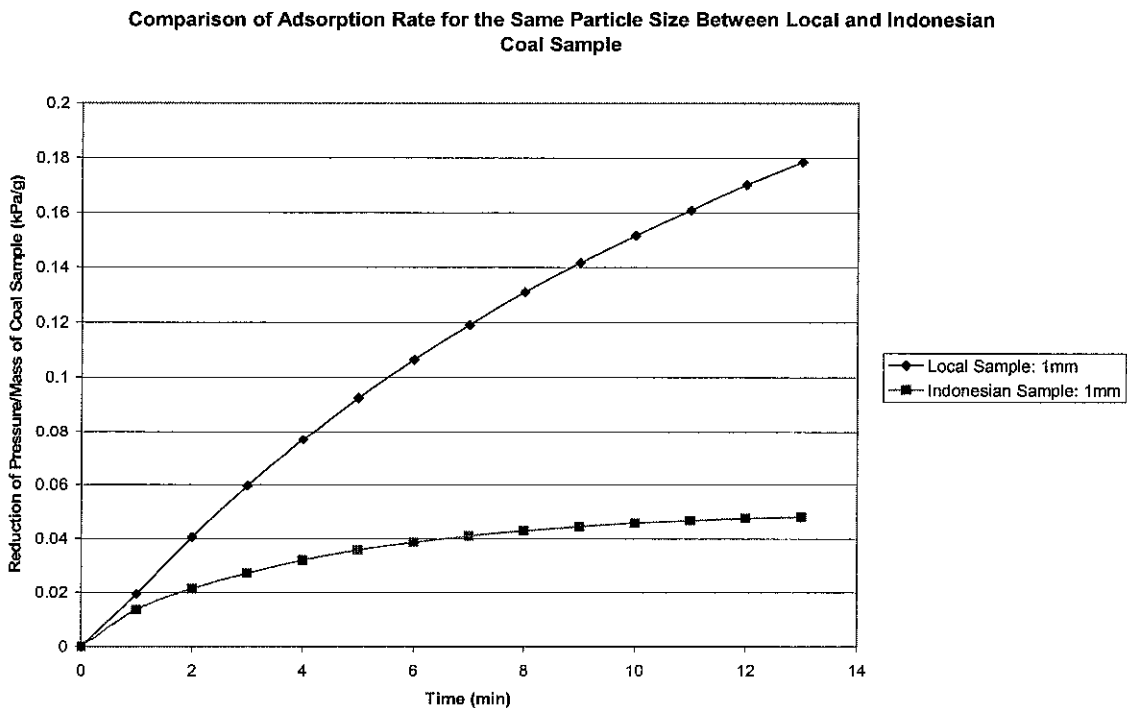


Figure 4.2: CO₂ Adsorption for local lignite and Indonesian bituminous (both of the same particle size of 1000μm and temperature of 40⁰C) at approximately 15kPa.

As observed above, the local coal sample, being a lower ranking coal sample, as compared to the Indonesian bituminous coal sample, gives a higher adsorption rate, hence confirming the literature review on the CO₂ adsorption in coals as a function of rank and composition discussed earlier. The same trend was observed for both of the temperatures and pH conditions experiments as well. This was also proven to be true in many experiments conducted by researchers for the purpose of CO₂ sequestration. This means that the prospects of implementing the CO₂ sequestration project in Malaysia is greater since the coal sample can adsorb CO₂ better.

4.3.5 Temperature Variation Experiment

The results for the temperature variation experiments are plotted and discussed below.

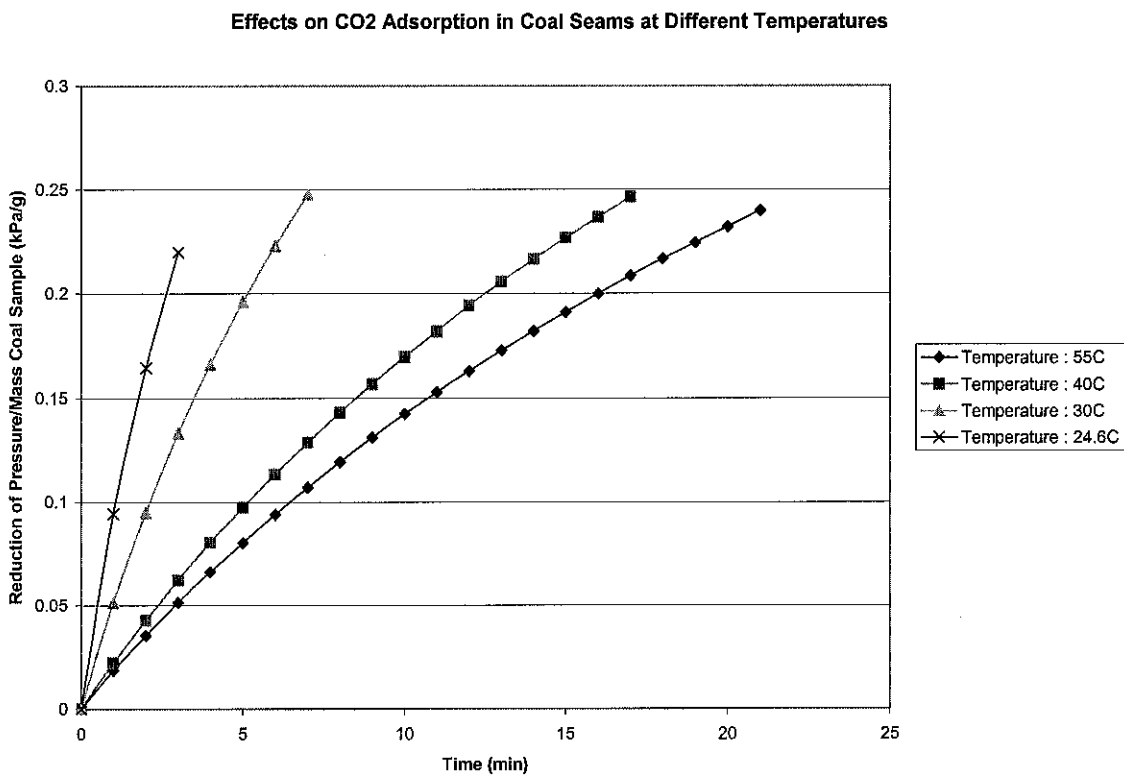


Figure 4.3: Effect on CO₂ Adsorption at Different Temperatures (24.6⁰C, 30⁰C, 40⁰C and 55⁰C) at 17kPa.

The temperature variation experiments were conducted at different temperatures of 24.6⁰C, 30⁰C, 40⁰C and 55⁰C. The plotted graph for these experiments is shown in Figure

4.3. From the graph, it can be observed that the effect of increasing the temperature is to decrease the equilibrium adsorption capacity of the coal samples.

For the sake of showing that the adsorption process reaches its equilibrium state (starts to level off), another set of experiments were conducted using higher pressure. The temperatures tested here are of 30⁰C and 40⁰C. The trend of the adsorption rate can also be seen here to be decreasing with higher temperatures. The data obtained is plotted below.

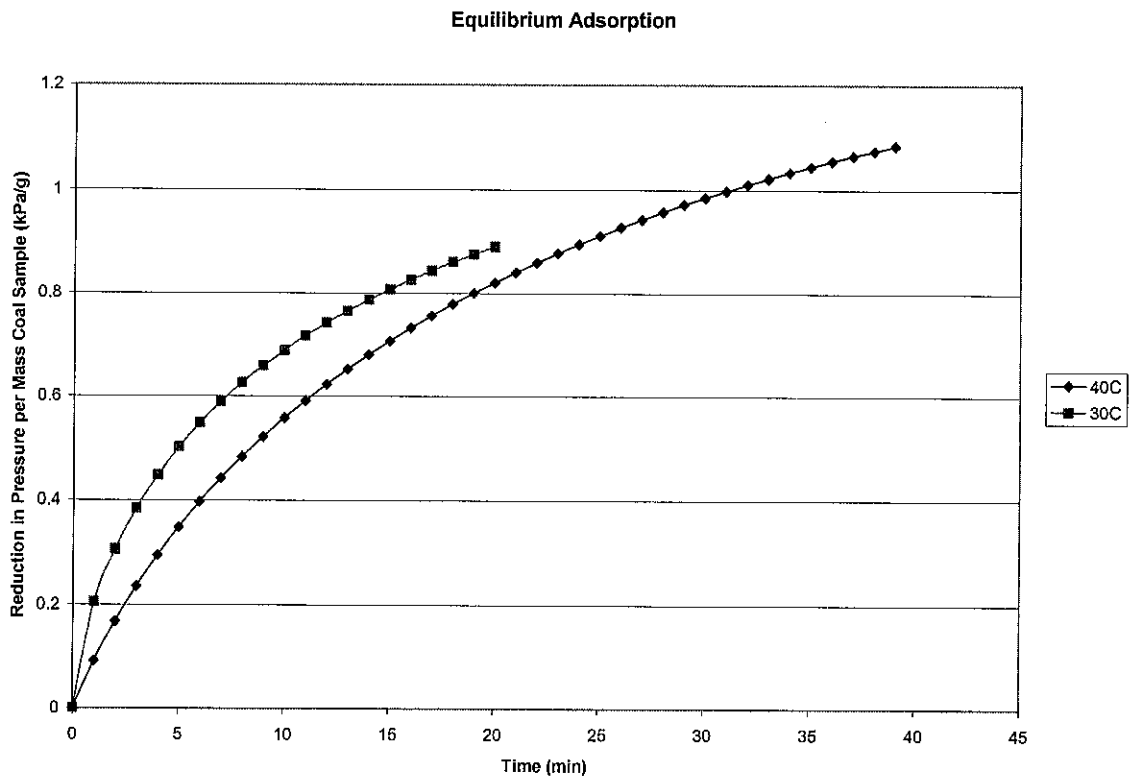


Figure 4.4: Effect on CO₂ Adsorption at Different Temperatures (30⁰C and 40⁰C) – Reaching Equilibrium at 60kPa.

This decrease can be explained using Langmuir, who was the first to propose a coherent theory of adsorption onto a flat surface based on a kinetic viewpoint, that there is a continual process of bombardment of molecules onto the surface and a corresponding evaporation (desorption) of molecules from the surface to maintain zero rate of accumulation at the surface at equilibrium. The assumptions of the Langmuir model are that the surface is homogenous, that is the adsorption energy is constant over all sites

(Do, Duong D.). It assumes that the adsorption on surface is localized, that is adsorbed atoms or molecules are adsorbed at definite, localized sites and each site can accommodate only one molecule or atom. The Langmuir theory is based on a kinetic principle, that is the rate of adsorption (which is the striking rate at the surface multiplied by a sticking coefficient, sometimes called the accommodation coefficient) is equal to the rate of desorption from the surface.

Equating the rates of adsorption and desorption, the following Langmuir isotherm was obtained.

$$\theta = \frac{bP}{1 + bP}$$

Where;

$$b = b_{\infty} \exp\left(\frac{Q}{R_g T}\right)$$

Here, Q is the heat of adsorption and is equal to the activation energy for desorption, E_d . The parameter b is called the affinity constant or Langmuir constant and is a measure of how strong an adsorbate molecule is attracted onto a surface.

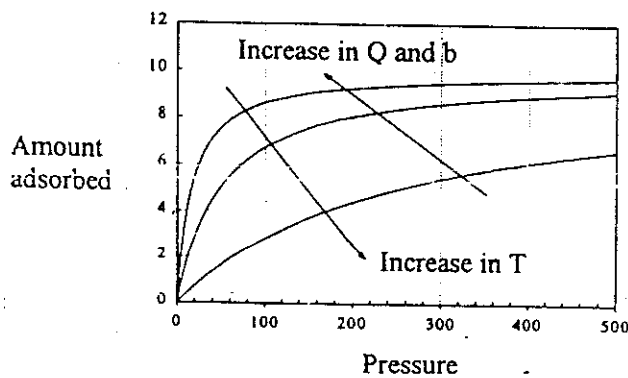
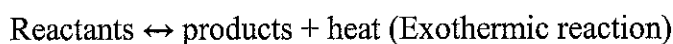


Figure 4.5: Behavior of the Langmuir Equation (Adsorption Analysis: Equilibria and Kinetics, Duong D. Do)

When the affinity constant b is larger, the surface is covered more with adsorbate molecules as a result of stronger affinity of adsorbate molecule towards the surface. Similarly, when the heat of adsorption Q increases, the adsorbed amount increases due to the higher energy barrier that adsorbed molecules have to overcome to evaporate back to the gas phase. Increase in the temperature will decrease the amount adsorbed at a given pressure. This is due to the greater energy acquired by the adsorbed molecule to evaporate.

This trend in the decreasing equilibrium adsorption capacity of the coal samples can also be explained from the Le Chatelier's principle. The change in temperature causes changes in the equilibrium constant K . A temperature rise will increase K for an endothermic process and decrease K for an exothermic reaction. Discussing this in our case point of view, the adsorption process of CO_2 onto the coal sample is an exothermic process which can be indicated by the following. Here, the endothermic reaction is also included for the purpose of discussions.



If we consider heat as a component in the equilibrium system, a rise in temperature "adds" heat to the system and a drop in temperature "removes" heat from the system. As with a change in any other component, the system shifts to reduce the effect of the change. Therefore, a temperature increase favors the endothermic (heat-absorbing) direction and a temperature decrease favors the exothermic (heat-releasing) direction. In our case, since the adsorption is an exothermic process, the production of heat will cause an imbalance in the equilibrium of the system. To attain back this equilibrium, the system will proceed in a different direction to achieve stability. Hence, with increasing temperatures, the heat in the system becomes much larger, causing the reaction to proceed more and more to the left side of the equation to attain equilibrium. This resulted in less adsorption to occur which explains the decrease in the equilibrium adsorption capacity observed from the graph.

Putting these reasoning into perspective, this means that otherwise equivalent, deeper, warmer seams will adsorb less CO₂ at a given pressure than shallower, cooler ones (K. Schroeder et al).

4.3.6 pH Variation Experiment

The results for the pH variation experiments are plotted and discussed below.

Effect of CO₂ Adsorption in Coal Seams at Different pH Conditions

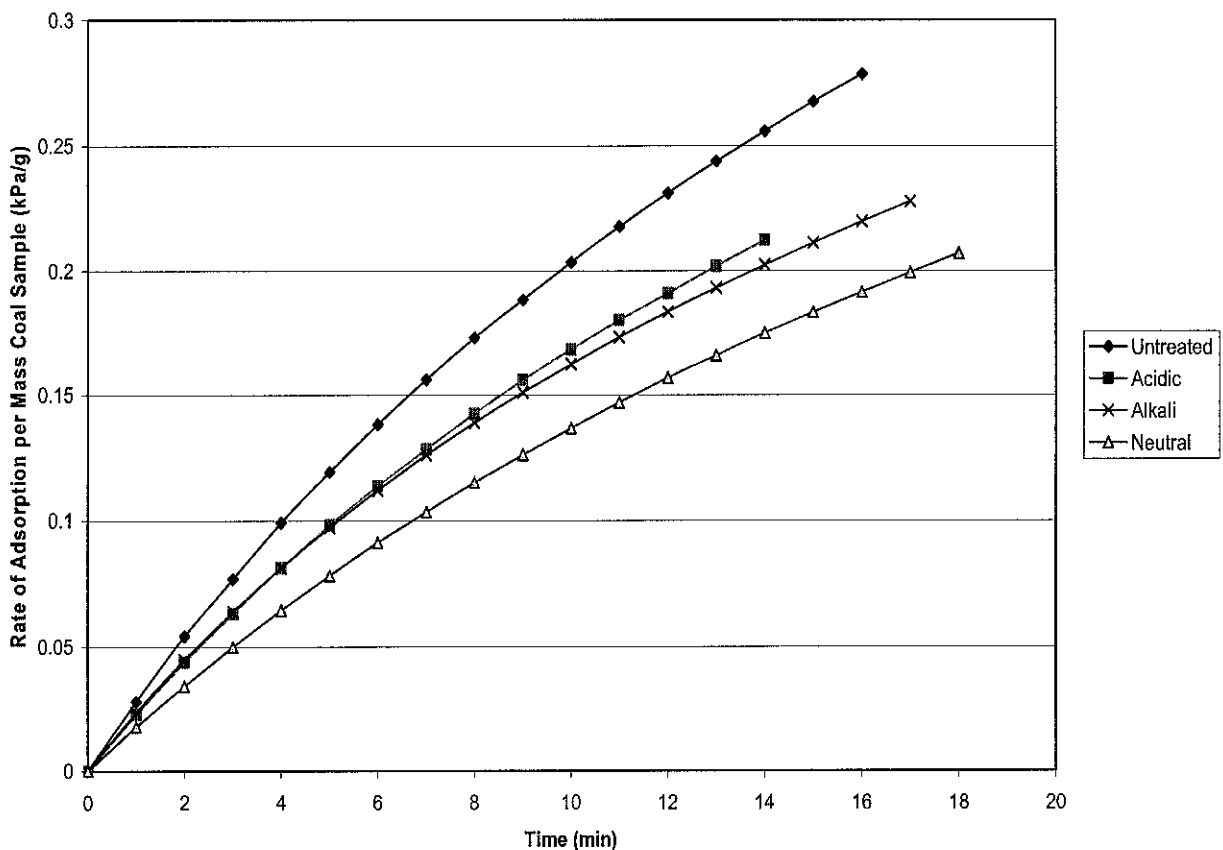


Figure 4.6: Effect on CO₂ Adsorption at Different pH Conditions (Acidic, Neutral, Alkali and Untreated) at 17kPa.

The variation of pH conditions experiments were conducted on coal samples that were treated with acid solution, distilled water (neutral), alkaline solution, and untreated sample. It can be observed that the untreated coal sample has the highest extent of adsorption capacity followed by the acidic, alkali and near neutral conditions.

From literature review, at pH of 9 (alkali), dissolved CO₂ exists as the carbonate ion and mineral carbonates are stable. At a pH of 2 (acidic) mineral carbonates dissolve, the CO₂ that can remain dissolved exists as H₂CO₃ and CO_{2(aq)} and CO_{2(gas)} is produced. The pH of an aqueous solution also affects the surface of a material it is in contact with. In the case of coal, at higher pH values, the carbonaceous surface, being in an environment above its isoelectric point, assumes a net negative charge. At lower pH value, the carbonaceous surface assumes a net positive charge. While a pH 9 will favor, and a pH 2 will disfavor, the aqueous capture of CO₂, the effect of being above, or below, the carbonaceous isoelectric point is not so obvious (K. Schroeder et. al).

The results obtained indicate lower extent of adsorption for those samples that were treated, regardless of treatment. Because all of these samples were oven dried whereas the untreated sample was not, it may not be valid to state that such mild drying would not affect the results. This is because moisture removal was known to affect the porosity and transport properties of coals, a phenomenon most commonly observed in lignite and sub-bituminous coals. However, the effects are usually mild for higher rank coals when the drying temperature is below 100⁰C (K. Schroeder et. al). Because of the uncertain effect of the drying, it is reasonable to limit the discussion of the pH effects to only three of the treated coal samples.

Comparing the rate of adsorption of CO₂ gas between the pH conditions of acidic, alkaline and neutral, it can be seen that the acidic conditions has the highest adsorption capacity. From literature, coal samples that were treated with acid were found to have reduced in its acid soluble minerals such as calcite. It was also found that the sample showed an ash reduction. If the removal of acid-soluble minerals resulted in increased accessible pore volume, then it is expected that the CO₂ capacity would increase. The ash content of base treated samples was found to have reduced by a smaller percentage. In this case, it seems more likely that any increase in capacity would be due to surface adsorbed NaOH. If water is also present, alkali metal hydroxides react with CO₂ to form carbonates. Whatever the mechanism, acid treatment appears to have a greater effect than the base or neutral treatments in these experiments (K. Schroeder et. al).

It should be noted here that from literature review, for experiments conducted using wet samples, the alkali treated samples showed a slightly higher adsorption rate as compared to the acid treated one. However, for similar experimental conditions, the opposite result was obtained if dry samples were used. This proves that the effect of the coal samples being above or below its carbonaceous isoelectric point is not so obvious. In other words, the rate of adsorption for acid and alkali treated samples will be more or less the same.

Nonetheless, whatever condition the samples were in (either wet or dry), the similarities found was that the untreated sample gave the highest rate while the neutral sample gave the lowest rate of adsorption. This phenomenon could be attributed to the fact that the untreated samples still retains its original moisture content which may have assisted the adsorption process. The high rate could also be attributed by the mineral phases present inside the coal through the process of mineral carbonate formation. As for the higher rate of adsorption of the acidic and alkali treated samples as compared to the neutral sample, this could be due to the fact that some of the acid/alkali soluble minerals present inside the coal had dissolved during the treatment process. This thus increased the accessible pore volume, and hence increases the adsorption rate slightly as compared to the neutral sample.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 CONCLUSIONS

The research on the effect of coal drying in adsorbing CO₂ at different temperature and pH was conducted on the local coal sample obtained from the coal mines of Sarawak. The research had also indulged in the process of determining the coal rank as well as other general properties of the coal.

In a nutshell, the research had covered the determination the coal sample characteristics through the moisture, ash, elemental compositions, mineral matter and the chemical elements analysis. The moisture content was found to be 37.4% while the ash percentage was 11.02%. The elemental composition of the sample coal was found to consist of carbon (56 – 60 %), hydrogen (3.9 – 4.3 %), nitrogen (1.89 – 1.95 %), sulfur (.28 – 0.4 %) and oxygen (22.4 – 26.3 %). The results of chemical elements analysis indicates the following compositions of the elements tested, calcium (3.14ppm), sodium (2.95ppm), magnesium (1.31ppm), potassium (12.40ppm), iron (23.94ppm), silica (436.34ppm) and aluminum (155.9ppm). The total mineral matter was found to be 12.09%.

Through these analyses, the coal samples were found to be of lignite type. It is known that rank has an effect on the amount of carbon dioxide that can be adsorbed in the coal seams. From literature review, coals of lignite type were found to be among those that have the highest tendency towards adsorbing CO₂ as compared to coals of other ranks.

For the experiments conducted for the purpose of studying the CO₂ gas adsorption patterns on local coal sample at different temperature, pH and particle sizes, the following results are obtained. For the temperature variation (24.6 °C, 30 °C, 40 °C and 55 °C), the rate of CO₂ gas adsorption was found to have decreased with increasing temperature. This is due to the entropy term in the free energy expression. In the variation of the pH conditions, it was observed that the untreated coal sample exhibit the highest

CO₂ gas adsorption as compared to the three treated coal samples (acidic, alkaline and near neutral each having a pH value of 0.51, 5.97 and 12.40 respectively). Between these three treated coal samples, acidic treated samples were found to be higher in its CO₂ gas adsorption followed by alkali and finally neutral. The high adsorption rate for the untreated sample may be due to the natural moisture contained inside the coal and also due to the mineral assistance via the mineral carbonate formation. The higher rate of adsorption for the acid and alkali treated sample as compared to the neutral sample could be due to the fact that some of the acid/alkali soluble minerals inside the coal had dissolved during the treatment process. This increased the accessible pore volume and hence increases its adsorption rate slightly. For the particle size variation, it was found that the CO₂ gas adsorption was higher for smaller coal particles (1000 μ m) as compared to larger particles (2000 μ m) due to larger surface area owned by the smaller particles. However, due to the coal's huge dominant internal surface area, this factor will have much of a significant effect in large scale projects.

Based on these findings, some general operating conditions for CO₂ sequestration can be predicted and tabulated. For example, efforts should be given to maintain the sequestration location's temperature at the desired optimum point. This is crucial since the adsorption process itself is known to be exothermic and it was clearly indicated from the experimental results that higher temperatures will cause unfavorable conditions for CO₂ adsorption to occur which in turn will lead to the incompletely filled coal seams. Similarly, the estimated costs of alternative sequestration scenarios, such as the sequestration of acid gases, need to take into account changes in the sequestration chemistry, such as increased pore capacity due to mineral dissolution or other surface changes.

5.2 RECOMMENDATIONS

These recommendations are made for the purpose of improving the current project for future researches. Several improvements can and should be made in terms of planning and carrying out the experiments so that better overall outcome of the project can be achieved.

Future researchers into this topic should familiarize themselves with the coal sample itself. The basic procedures for determining the type of coal and its other properties should be known prior to the start of the research. This is to ensure that the researcher is well aware of the parameters and the expected results that he/she is searching for when conducting the experiments.

It is highly recommended that the test or experiments conducted on the coal sample be done in accordance with the standard procedures given in the American Standard for Testing Materials (ASTM) so as to ensure that accurate analysis of the coal sample can be obtained. The utilization of this standard will also allow comparison be done on a standard basis between the results obtained with the ones from literature review.

It is also recommended that the experimental set-up be improved so as to enable better adsorption process to take place and be monitored. The utilized experimental set-up was problematic in the sense that the coal sample had to be taken out of the sample cell and weighed separately after each experiment to determine its mass. This created some discrepancies in the mass value since some unavoidable loss of the coal sample will occur during the transfer, hence creating opportunities for errors to occur. A new experimental set-up should be utilized so as not to repeat the errors in future researches.

For future researches, it is highly recommended that the desorption rate of CH_4 be studied upon at different parameter variations. Since the main attraction of CO_2 sequestration in coal seams was because it enhances the CH_4 production in coal beds, it is only logical that this matter was thoroughly investigated.

It is also recommended that the investigation of the role of minerals in assisting the CO₂ adsorption on coal seams be done. This can be carried out by testing the adsorption rate of coal samples of the same rank from different sources. The mineral content of the coal samples should be first determined and any relationship between the mineral content and the rate of adsorption can then be studied upon. Since the exact role of minerals has not yet been determined, it should be interesting to see if there are any significant correlations or connections that can be established between these two.

Although from an economic point of view, the project for the purpose of CO₂ sequestration solely may not be feasible for a small country like Malaysia, at the very least, the researches conducted can be utilized to enhance the production of CH₄ gases from the coal mines. Through this, we will be able to kill two birds with one stone. Not only will we be able to increase the production of CH₄, which are economically feasible, we will also be doing our part in helping to reduce the CO₂ concentration in the atmosphere and in doing so, keep the global warming effects at bay.

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APPENDICES

APPENDIX A:
CO₂ ADSORPTION
EXPERIMENTAL DATA

TABLE A1: Experimental Data for the Particle Size Variation on CO₂ Adsorption – Particle Size 1000µm.

T = 40°C

Mass of coal sample: 95g

Sample coal size: 1000µm

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure (kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|-----------------------------|---|
| 0 | 17.19 | 17 | 0 | 0 |
| 1 | 15.34 | 15.15 | 1.85 | 0.019473684 |
| 2 | 13.33 | 13.14 | 3.86 | 0.040631579 |
| 3 | 11.52 | 11.33 | 5.67 | 0.059684211 |
| 4 | 9.89 | 9.7 | 7.3 | 0.076842105 |
| 5 | 8.42 | 8.23 | 8.77 | 0.092315789 |
| 6 | 7.09 | 6.9 | 10.1 | 0.106315789 |
| 7 | 5.88 | 5.69 | 11.31 | 0.119052632 |
| 8 | 4.75 | 4.56 | 12.44 | 0.130947368 |
| 9 | 3.74 | 3.55 | 13.45 | 0.141578947 |
| 10 | 2.79 | 2.6 | 14.4 | 0.151578947 |
| 11 | 1.9 | 1.71 | 15.29 | 0.160947368 |
| 12 | 1.03 | 0.84 | 16.16 | 0.170105263 |
| 13 | 0.24 | 0.05 | 16.95 | 0.178421053 |

TABLE A2: Experimental Data for the Particle Size Variation on CO₂ Adsorption – Particle Size 2000µm.

T = 40°C

Mass of coal sample: 95g

Sample coal size: 2000µm

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure (kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|-----------------------------|---|
| 0 | 17.08 | 17 | 0 | 0 |
| 1 | 15.55 | 15.47 | 1.53 | 0.016105263 |
| 2 | 14.12 | 14.04 | 2.96 | 0.031157895 |
| 3 | 12.77 | 12.69 | 4.31 | 0.045368421 |
| 4 | 11.52 | 11.44 | 5.56 | 0.058526316 |
| 5 | 10.33 | 10.25 | 6.75 | 0.071052632 |
| 6 | 9.14 | 9.06 | 7.94 | 0.083578947 |
| 7 | 8.15 | 8.07 | 8.93 | 0.094 |
| 8 | 7.12 | 7.04 | 9.96 | 0.104842105 |
| 9 | 6.15 | 6.07 | 10.93 | 0.115052632 |
| 10 | 5.24 | 5.16 | 11.84 | 0.124631579 |
| 11 | 4.34 | 4.26 | 12.74 | 0.134105263 |
| 12 | 3.5 | 3.42 | 13.58 | 0.142947368 |
| 13 | 2.7 | 2.62 | 14.38 | 0.151368421 |
| 14 | 1.94 | 1.86 | 15.14 | 0.159368421 |
| 15 | 1.2 | 1.12 | 15.88 | 0.167157895 |
| 16 | 0.51 | 0.43 | 16.57 | 0.174421053 |

TABLE A3: Experimental Data for the Temperature Variation on CO₂ Adsorption – Temperature at 55^oC

T = 55^oC

Mass of coal sample: 70.05g

Sample coal size: 1000 μ m

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure(kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|----------------------------|---|
| 0 | 17.76 | 17 | 0 | 0 |
| 1 | 16.48 | 15.72 | 1.28 | 0.018272662 |
| 2 | 15.29 | 14.53 | 2.47 | 0.035260528 |
| 3 | 14.17 | 13.41 | 3.59 | 0.051249108 |
| 4 | 13.12 | 12.36 | 4.64 | 0.066238401 |
| 5 | 12.14 | 11.38 | 5.62 | 0.080228408 |
| 6 | 11.18 | 10.42 | 6.58 | 0.093932905 |
| 7 | 10.26 | 9.5 | 7.5 | 0.107066381 |
| 8 | 9.41 | 8.65 | 8.35 | 0.119200571 |
| 9 | 8.59 | 7.83 | 9.17 | 0.130906495 |
| 10 | 7.79 | 7.03 | 9.97 | 0.142326909 |
| 11 | 7.05 | 6.29 | 10.71 | 0.152890792 |
| 12 | 6.35 | 5.59 | 11.41 | 0.162883655 |
| 13 | 5.67 | 4.91 | 12.09 | 0.172591006 |
| 14 | 5.02 | 4.26 | 12.74 | 0.181870093 |
| 15 | 4.38 | 3.62 | 13.38 | 0.191006424 |
| 16 | 3.76 | 3 | 14 | 0.199857245 |
| 17 | 3.16 | 2.4 | 14.6 | 0.208422555 |
| 18 | 2.59 | 1.83 | 15.17 | 0.2165596 |
| 19 | 2.04 | 1.28 | 15.72 | 0.22441135 |
| 20 | 1.51 | 0.75 | 16.25 | 0.231977159 |
| 21 | 0.96 | 0.2 | 16.8 | 0.239828694 |

TABLE A4: Experimental Data for the Temperature Variation on CO₂ Adsorption – Temperature at 40°C

T = 40°C

Mass of coal sample: 68.69g

Sample coal size: 1000µm

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure (kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|-----------------------------|---|
| 0 | 17.87 | 17 | 0 | 0 |
| 1 | 16.35 | 15.48 | 1.52 | 0.022128403 |
| 2 | 14.94 | 14.07 | 2.93 | 0.042655408 |
| 3 | 13.6 | 12.73 | 4.27 | 0.062163343 |
| 4 | 12.34 | 11.47 | 5.53 | 0.080506624 |
| 5 | 11.18 | 10.31 | 6.69 | 0.097394089 |
| 6 | 10.09 | 9.22 | 7.78 | 0.113262484 |
| 7 | 9.04 | 8.17 | 8.83 | 0.128548551 |
| 8 | 8.04 | 7.17 | 9.83 | 0.143106711 |
| 9 | 7.11 | 6.24 | 10.76 | 0.1566458 |
| 10 | 6.23 | 5.36 | 11.64 | 0.169456981 |
| 11 | 5.38 | 4.51 | 12.49 | 0.181831417 |
| 12 | 4.55 | 3.68 | 13.32 | 0.193914689 |
| 13 | 3.75 | 2.88 | 14.12 | 0.205561217 |
| 14 | 3 | 2.13 | 14.87 | 0.216479837 |
| 15 | 2.29 | 1.42 | 15.58 | 0.22681613 |
| 16 | 1.61 | 0.74 | 16.26 | 0.236715679 |
| 17 | 0.94 | 0.07 | 16.93 | 0.246469646 |

TABLE A5: Experimental Data for the Temperature Variation on CO₂ Adsorption – Temperature at 30°C

T = 30°C

Mass of coal sample: 67.77g

Sample coal size: 1000µm

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure(kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|----------------------------|---|
| 0 | 17.42 | 17 | 0 | 0 |
| 1 | 13.94 | 13.52 | 3.48 | 0.051350155 |
| 2 | 10.98 | 10.56 | 6.44 | 0.095027298 |
| 3 | 8.41 | 7.99 | 9.01 | 0.132949683 |
| 4 | 6.16 | 5.74 | 11.26 | 0.166150214 |
| 5 | 4.14 | 3.72 | 13.28 | 0.195956913 |
| 6 | 2.31 | 1.89 | 15.11 | 0.222960012 |
| 7 | 0.64 | 0.22 | 16.78 | 0.247602184 |

TABLE A6: Experimental Data for the Temperature Variation on CO₂ Adsorption – Temperature at 24.5°C

T = 24.6°C

Mass of coal sample: 67.63g

Sample coal size: 1000µm

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure(kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|----------------------------|---|
| 0 | 17.26 | 17 | 0 | 0 |
| 1 | 10.88 | 10.62 | 6.38 | 0.094336833 |
| 2 | 6.14 | 5.88 | 11.12 | 0.164424072 |
| 3 | 2.39 | 2.13 | 14.87 | 0.219872837 |

TABLE A7: Experimental Data for the pH Condition Variation on CO₂ Adsorption – Untreated Conditions

T = 40°C
Mass of coal sample: 60g
Sample coal size: 1000µm
pH Condition: Untreated

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure (kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|-----------------------------|---|
| 0 | 17.76 | 17 | 0 | 0 |
| 1 | 16.09 | 15.33 | 1.67 | 0.027833333 |
| 2 | 14.51 | 13.75 | 3.25 | 0.054166667 |
| 3 | 13.14 | 12.38 | 4.62 | 0.077 |
| 4 | 11.81 | 11.05 | 5.95 | 0.099166667 |
| 5 | 10.59 | 9.83 | 7.17 | 0.1195 |
| 6 | 9.46 | 8.7 | 8.3 | 0.138333333 |
| 7 | 8.39 | 7.63 | 9.37 | 0.156166667 |
| 8 | 7.38 | 6.62 | 10.38 | 0.173 |
| 9 | 6.46 | 5.7 | 11.3 | 0.188333333 |
| 10 | 5.56 | 4.8 | 12.2 | 0.203333333 |
| 11 | 4.7 | 3.94 | 13.06 | 0.217666667 |
| 12 | 3.9 | 3.14 | 13.86 | 0.231 |
| 13 | 3.13 | 2.37 | 14.63 | 0.243833333 |
| 14 | 2.41 | 1.65 | 15.35 | 0.255833333 |
| 15 | 1.71 | 0.95 | 16.05 | 0.2675 |
| 16 | 1.05 | 0.29 | 16.71 | 0.2785 |

TABLE A8: Experimental Data for the pH Condition Variation on CO₂ Adsorption – Acidic Conditions (pH of 0.51)

T = 40°C

Mass of coal sample: 80g

Sample coal size: 1000µm

pH Condition: Acidic

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure (kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|-----------------------------|---|
| 0 | 17.95 | 17 | 0 | 0 |
| 1 | 16.14 | 15.19 | 1.81 | 0.022625 |
| 2 | 14.46 | 13.51 | 3.49 | 0.043625 |
| 3 | 12.9 | 11.95 | 5.05 | 0.063125 |
| 4 | 11.44 | 10.49 | 6.51 | 0.081375 |
| 5 | 10.1 | 9.15 | 7.85 | 0.098125 |
| 6 | 8.84 | 7.89 | 9.11 | 0.113875 |
| 7 | 7.68 | 6.73 | 10.27 | 0.128375 |
| 8 | 6.55 | 5.6 | 11.4 | 0.1425 |
| 9 | 5.48 | 4.53 | 12.47 | 0.155875 |
| 10 | 4.5 | 3.55 | 13.45 | 0.168125 |
| 11 | 3.55 | 2.6 | 14.4 | 0.18 |
| 12 | 2.67 | 1.72 | 15.28 | 0.191 |
| 13 | 1.8 | 0.85 | 16.15 | 0.201875 |
| 14 | 0.98 | 0.03 | 16.97 | 0.212125 |

TABLE A9: Experimental Data for the pH Condition Variation on CO₂ Adsorption – Alkaline Conditions (pH of 12.40)

T = 40°C

Mass of coal sample: 80g

Sample coal size: 1000µm

pH Condition: Alkali

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure(kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|----------------------------|---|
| 0 | 17.81 | 17 | 0 | 0 |
| 1 | 16.06 | 15.25 | 1.75 | 0.023562677 |
| 2 | 14.49 | 13.68 | 3.32 | 0.044701764 |
| 3 | 13.07 | 12.26 | 4.74 | 0.063821193 |
| 4 | 11.77 | 10.96 | 6.04 | 0.081324896 |
| 5 | 10.58 | 9.77 | 7.23 | 0.097347516 |
| 6 | 9.48 | 8.67 | 8.33 | 0.112158341 |
| 7 | 8.43 | 7.62 | 9.38 | 0.126295947 |
| 8 | 7.49 | 6.68 | 10.32 | 0.138952471 |
| 9 | 6.6 | 5.79 | 11.21 | 0.150935775 |
| 10 | 5.76 | 4.95 | 12.05 | 0.16224586 |
| 11 | 4.95 | 4.14 | 12.86 | 0.173152013 |
| 12 | 4.18 | 3.37 | 13.63 | 0.183519591 |
| 13 | 3.46 | 2.65 | 14.35 | 0.193213949 |
| 14 | 2.78 | 1.97 | 15.03 | 0.202369732 |
| 15 | 2.13 | 1.32 | 15.68 | 0.211121583 |
| 16 | 1.5 | 0.69 | 16.31 | 0.219604147 |
| 17 | 0.9 | 0.09 | 16.91 | 0.227682779 |

TABLE A10: Experimental Data for the pH Condition Variation on CO₂ Adsorption – Near Neutral Conditions (pH of 5.97)

T = 40°C

Mass of coal sample: 80g

Sample coal size: 1000µm

pH Condition: Near - Neutral

| Time (min) | Pressure (kPa) | Corrected Data (kPa) | Reduction of Pressure (kPa) | Reduction of Pressure per Mass Coal (kPa/g) |
|------------|----------------|----------------------|-----------------------------|---|
| 0 | 17.36 | 17 | 0 | 0 |
| 1 | 15.95 | 15.59 | 1.41 | 0.017625 |
| 2 | 14.64 | 14.28 | 2.72 | 0.034 |
| 3 | 13.38 | 13.02 | 3.98 | 0.04975 |
| 4 | 12.2 | 11.84 | 5.16 | 0.0645 |
| 5 | 11.1 | 10.74 | 6.26 | 0.07825 |
| 6 | 10.05 | 9.69 | 7.31 | 0.091375 |
| 7 | 9.08 | 8.72 | 8.28 | 0.1035 |
| 8 | 8.15 | 7.79 | 9.21 | 0.115125 |
| 9 | 7.26 | 6.9 | 10.1 | 0.12625 |
| 10 | 6.42 | 6.06 | 10.94 | 0.13675 |
| 11 | 5.6 | 5.24 | 11.76 | 0.147 |
| 12 | 4.82 | 4.46 | 12.54 | 0.15675 |
| 13 | 4.09 | 3.73 | 13.27 | 0.165875 |
| 14 | 3.37 | 3.01 | 13.99 | 0.174875 |
| 15 | 2.69 | 2.33 | 14.67 | 0.183375 |
| 16 | 2.05 | 1.69 | 15.31 | 0.191375 |
| 17 | 1.42 | 1.06 | 15.94 | 0.19925 |
| 18 | 0.81 | 0.45 | 16.55 | 0.206875 |

APPENDIX B:
COAL ANALYSIS EXPERIMENTAL
DATA
&
ASTM STANDARDS

APPENDIX B

LIST OF APPENDICES:

Arranged in the following order:

1. Results from Atomic Absorption Spectrometer (AAS)
2. Results from CHNS-O Analysis
3. ASTM Standards:
 - a. Standard Classification of Coals by Rank
 - b. Standard Test Method for Moisture in the Analysis Sample of Coal and Coke
 - c. Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption

Analysis Mode :Flame/Autosampler
 Analysis Name :Metal content in coal sample analysis
 Comment :Suhana Muhamad

Meas. Date :9/14/04 4:05 PM
 Element :Si

| Sample ID :STD1 | | Sample Name: | | |
|-----------------|------------|--------------|--------|---------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.00 | 0.0001 | -0.0015 |
| Mean | -- | -- | 0.0001 | -0.0015 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

| Sample ID :STD2 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 20.00 | 0.0473 | 0.0016 |
| Mean | -- | -- | 0.0473 | 0.0016 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

| Sample ID :STD3 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 40.00 | 0.0913 | 0.0027 |
| Mean | -- | -- | 0.0913 | 0.0027 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

| Sample ID :STD4 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 80.00 | 0.1769 | 0.0067 |
| Mean | -- | -- | 0.1769 | 0.0067 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

Coefficient :K3---
 K2---
 K1=2.201143E-003
 K0=1.860001E-003
 Corr.Coeff. :0.9998

| Sample ID :UNK-001 | | Sample Name:sample containing coal | | |
|--------------------|------------------|------------------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 436.34 | 436.34 | 0.9623 | 0.0500 |
| Mean | 436.34 | 436.34 | 0.9623 | 0.0500 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD | 0.00 | 0.00 | 0.00 | 0.00 |

| Sample ID :UNK-002 | | Sample Name:sample (blanks) | | |
|--------------------|------------------|-----------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 386.18 | 386.18 | 0.8519 | 0.0415 |
| Mean | 386.18 | 386.18 | 0.8519 | 0.0415 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD | 0.00 | 0.00 | 0.00 | 0.00 |

Analysis Mode :Flame/Autosampler
 Analysis Name :Metal content in coal sample analysis
 Comment :Suhana Muhamad

Meas. Date :9/14/04 3:58 PM

Element :AL

| Sample ID :STD1 | | Sample Name: | | |
|-----------------|------------|--------------|---------|---------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.00 | -0.0002 | -0.0061 |
| Mean | -- | -- | -0.0002 | -0.0061 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

| Sample ID :STD2 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 10.00 | 0.0482 | 0.0002 |
| Mean | -- | -- | 0.0482 | 0.0002 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

| Sample ID :STD3 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 20.00 | 0.0979 | 0.0079 |
| Mean | -- | -- | 0.0979 | 0.0079 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

| Sample ID :STD4 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 40.00 | 0.1901 | 0.0181 |
| Mean | -- | -- | 0.1901 | 0.0181 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

Coefficient :K3---
 K2---
 K1=4.758857E-003
 K0=7.200008E-004
 Corr.Coeff. :0.9999

| Sample ID :UNK-001 | | Sample Name:sample containing coal | | |
|--------------------|------------------|------------------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 155.79 | 155.79 | 0.7421 | 0.1725 |
| Mean | 155.79 | 155.79 | 0.7421 | 0.1725 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD | 0.00 | 0.00 | 0.00 | 0.00 |

| Sample ID :UNK-002 | | Sample Name:sample (blanks) | | |
|--------------------|------------------|-----------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 126.43 | 126.43 | 0.6024 | 0.0853 |
| Mean | 126.43 | 126.43 | 0.6024 | 0.0853 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD | 0.00 | 0.00 | 0.00 | 0.00 |

Analysis Mode :Flame/Autosampler
 Analysis Name :Metal content in coal sample analysis
 Comment :Suhana Muhamad

Meas. Date :9/14/04 10:53 AM

Element :Ca

| Sample ID :STD1 | | Sample Name: | | |
|-----------------|------------|--------------|--------|---------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.00 | 0.0004 | -0.0067 |
| Mean | -- | -- | 0.0004 | -0.0067 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD (%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD2 | | Sample Name: | | |
|-----------------|------------|--------------|--------|---------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.50 | 0.0262 | -0.0013 |
| Mean | -- | -- | 0.0262 | -0.0013 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD (%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD3 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 1.00 | 0.0507 | 0.0082 |
| Mean | -- | -- | 0.0507 | 0.0082 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD (%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD4 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 2.00 | 0.0847 | 0.0068 |
| Mean | -- | -- | 0.0847 | 0.0068 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD (%) | -- | -- | 0.00 | 0.00 |

Coefficient :K3---
 K2---
 K1=4.180572E-002
 K0=3.920000E-003

Corr.Coeff. :0.9939

| Sample ID :UNK-001 | | Sample Name:sample containing coal | | |
|--------------------|------------------|------------------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 3.14 | 3.14 | 0.1352 | 0.0057 |
| Mean | 3.14 | 3.14 | 0.1352 | 0.0057 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD (%) | 0.00 | 0.00 | 0.00 | 0.00 |

| Sample ID :UNK-002 | | Sample Name:sample (blanks) | | |
|--------------------|------------------|-----------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 6.01 | 6.01 | 0.2551 | 0.0112 |
| Mean | 6.01 | 6.01 | 0.2551 | 0.0112 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD (%) | 0.00 | 0.00 | 0.00 | 0.00 |

Analysis Mode :Flame/Autosampler
 Analysis Name :Metal content in coal sample analysis
 Comment :Suhana Muhamad

Meas. Date :9/14/04 11:20 AM
 Element :Na

| Sample ID :STD1 | | Sample Name: | | |
|-----------------|------------|--------------|---------|---------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.00 | -0.0002 | -0.0005 |
| Mean | -- | -- | -0.0002 | -0.0005 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD | -- | -- | 0.00 | 0.00 |

| Sample ID :STD2 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.20 | 0.0055 | 0.0015 |
| Mean | -- | -- | 0.0055 | 0.0015 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD (%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD3 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.40 | 0.0117 | 0.0024 |
| Mean | -- | -- | 0.0117 | 0.0024 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD (%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD4 | | Sample Name: | | |
|---------------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.80 | 0.0272 | 0.0065 |
| Mean | -- | -- | 0.0272 | 0.0065 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD (%) | -- | -- | 0.00 | 0.00 |
| Coefficient :K3--- | | | | |
| K2--- | | | | |
| K1=3.307143E-002 | | | | |
| K0=2.999998E-004 | | | | |
| Corr.Coeff. :0.9905 | | | | |

| Sample ID :UNK-001 | | Sample Name:sample containing coal | | |
|--------------------|------------------|------------------------------------|--------|----------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 2.95 | 2.95 | 0.0978 | 0.6047 B |
| Mean | 2.95 | 2.95 | 0.0978 | 0.6047 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD (%) | 0.00 | 0.00 | 0.00 | 0.00 |

| Sample ID :UNK-002 | | Sample Name:sample (blanks) | | |
|--------------------|------------------|-----------------------------|--------|----------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 12.56 | 12.56 | 0.4156 | 0.2253 B |
| Mean | 12.56 | 12.56 | 0.4156 | 0.2253 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD (%) | 0.00 | 0.00 | 0.00 | 0.00 |

Analysis Mode :Flame/Autosampler
 Analysis Name :Metal content in coal sample analysis
 Comment :Suhana Muhamad

Meas. Date :9/14/04 11:14 AM

Element :Mg

| Sample ID :STD1 | | Sample Name: | | |
|-----------------|------------|--------------|---------|---------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.00 | -0.0010 | -0.0002 |
| Mean | -- | -- | -0.0010 | -0.0002 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD2 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.10 | 0.0404 | 0.0050 |
| Mean | -- | -- | 0.0404 | 0.0050 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD3 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.20 | 0.1360 | 0.0170 |
| Mean | -- | -- | 0.1360 | 0.0170 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD4 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.40 | 0.2835 | 0.0354 |
| Mean | -- | -- | 0.2835 | 0.0354 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

Coefficient :K3---
 K2---
 K1=7.352285E-001
 K0=-1.394000E-002
 Corr.Coeff. :0.9942

| Sample ID :UNK-001 | | Sample Name:sample containing coal | | |
|--------------------|------------------|------------------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 1.31 | 1.31 | 0.9483 | 0.8499 |
| Mean | 1.31 | 1.31 | 0.9483 | 0.8499 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD(%) | 0.00 | 0.00 | 0.00 | 0.00 |

| Sample ID :UNK-002 | | Sample Name:sample (blanks) | | |
|--------------------|------------------|-----------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 0.98 | 0.98 | 0.7053 | 1.1522 |
| Mean | 0.98 | 0.98 | 0.7053 | 1.1522 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD(%) | 0.00 | 0.00 | 0.00 | 0.00 |

Analysis Mode :Flame/Autosampler
 Analysis Name :Metal content in coal sample analysis
 Comment :Suhana Muhamad

Meas. Date :9/14/04 11:07 AM

Element :K

| Sample ID :STD1 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.00 | 0.0007 | 0.0018 |
| Mean | -- | -- | 0.0007 | 0.0018 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD2 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.25 | 0.0431 | 0.0084 |
| Mean | -- | -- | 0.0431 | 0.0084 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD3 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.50 | 0.0625 | 0.0109 |
| Mean | -- | -- | 0.0625 | 0.0109 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD4 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 1.00 | 0.0968 | 0.0155 |
| Mean | -- | -- | 0.0968 | 0.0155 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

Coefficient :K3=--
 K2=--
 K1=9.137143E-002
 K0=1.080000E-002

Corr.Coe1. :0.9730

| Sample ID :UNK-001 | | Sample Name:sample containing coal | | |
|--------------------|------------------|------------------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 12.40 | 12.40 | 1.1442 | 0.3195 |
| Mean | 12.40 | 12.40 | 1.1442 | 0.3195 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD(%) | 0.00 | 0.00 | 0.00 | 0.00 |

| Sample ID :UNK-002 | | Sample Name:sample (blanks) | | |
|--------------------|------------------|-----------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 10.63 | 10.63 | 0.9823 | 0.1790 |
| Mean | 10.63 | 10.63 | 0.9823 | 0.1790 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD(%) | 0.00 | 0.00 | 0.00 | 0.00 |

Detail Table

9/14/04 11:00 AM

Analysis Mode :Flame/Autosampler
 Analysis Name :Metal content in coal sample analysis
 Comment :Suhana Muhamad

Meas. Date :9/14/04 11:00 AM

Element :Fe

| Sample ID :STD1 | | Sample Name: | | |
|-----------------|------------|--------------|---------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 0.00 | -0.0003 | 0.0000 |
| Mean | -- | -- | -0.0003 | 0.0000 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD2 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 1.00 | 0.0304 | 0.0010 |
| Mean | -- | -- | 0.0304 | 0.0010 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

| Sample ID :STD3 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 2.00 | 0.0523 | 0.0024 |
| Mean | -- | -- | 0.0523 | 0.0024 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

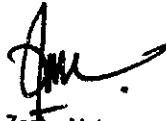
| Sample ID :STD4 | | Sample Name: | | |
|-----------------|------------|--------------|--------|--------|
| No. | Corr.Conc. | Conc. (ppm) | ABS | REF |
| 1 | -- | 4.00 | 0.1377 | 0.0073 |
| Mean | -- | -- | 0.1377 | 0.0073 |
| SD | -- | -- | 0.0000 | 0.0000 |
| RSD(%) | -- | -- | 0.00 | 0.00 |

Coefficient :K3---
 K2---
 K1=3.435714E-002
 K0=-5.100001E-003
 Corr.Coeff. :0.9913

| Sample ID :UNK-001 | | Sample Name:sample containing coal | | |
|--------------------|------------------|------------------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 23.94 | 23.94 | 0.8175 | 0.1356 |
| Mean | 23.94 | 23.94 | 0.8175 | 0.1356 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD(%) | 0.00 | 0.00 | 0.00 | 0.00 |

| Sample ID :UNK-002 | | Sample Name:sample (blanks) | | |
|--------------------|------------------|-----------------------------|--------|--------|
| No. | Corr.Conc. (ppm) | Conc. (ppm) | ABS | REF |
| 1 | 5.34 | 5.34 | 0.1782 | 0.0128 |
| Mean | 5.34 | 5.34 | 0.1782 | 0.0128 |
| SD | 0.00 | 0.00 | 0.0000 | 0.0000 |
| RSD(%) | 0.00 | 0.00 | 0.00 | 0.00 |

| | | |
|--|---|-----------------|
| COAL 43 Type | WT=0.583 mg Chan # 1 | 09:31 Oct-08-04 |
| 56.31% H = 4.071% | N = 1.900% S = 0.364% | |
| 100 Peak= 3836 Time = 180 Peak= 1861 | Time = 100 Peak= 380 Time = 150 Peak= 74 | |
| 160 Blk =0.008 Calib=1.0647 Blk =0.088 | Calib=0.9934 Blk =0.038 Calib=1.0643 Blk =0.001 | |
| COAL 44 Type | WT=0.603 mg Chan # 1 | 09:34 Oct-08-04 |
| 58.46% H = 4.285% | N = 1.957% S = 0.402% | |
| 100 Peak= 3948 Time = 180 Peak= 2006 | Time = 100 Peak= 385 Time = 150 Peak= 43 | |
| 160 Blk =0.008 Calib=1.0647 Blk =0.088 | Calib=0.9934 Blk =0.038 Calib=1.0643 Blk =0.001 | |
| COAL 45 Type | WT=0.581 mg Chan # 1 | 09:37 Oct-08-04 |
| 57.74% H = 4.330% | N = 1.922% S = 0.379% | |
| 100 Peak= 3766 Time = 180 Peak= 2004 | Time = 100 Peak= 369 Time = 150 Peak= 32 | |
| 160 Blk =0.008 Calib=1.0647 Blk =0.088 | Calib=0.9934 Blk =0.038 Calib=1.0643 Blk =0.001 | |
| COAL 46 Type | WT=0.604 mg Chan # 1 | 09:41 Oct-08-04 |
| 56.17% H = 3.909% | N = 1.888% S = 0.300% | |
| 100 Peak= 3827 Time = 180 Peak= 1868 | Time = 100 Peak= 374 Time = 150 Peak= 26 | |
| 160 Blk =0.008 Calib=1.0647 Blk =0.088 | Calib=0.9934 Blk =0.038 Calib=1.0643 Blk =0.001 | |
| COAL 47 Type | WT=0.602 mg Chan # 1 | 09:44 Oct-08-04 |
| 60.24% H = 4.200% | N = 1.889% S = 0.279% | |
| 100 Peak= 4278 Time = 180 Peak= 2051 | Time = 100 Peak= 381 Time = 150 Peak= 26 | |
| 160 Blk =0.008 Calib=1.0647 Blk =0.088 | Calib=0.9934 Blk =0.038 Calib=1.0643 Blk =0.001 | |

 12/10/04.
 11:00am
 Zsaba Mohammad
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 Chemical Engineering Programme
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Standard Classification of Coals by Rank¹

This standard is issued under the fixed designation D 388; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This standard covers the classification of coals by rank, that is, according to their degree of metamorphism, or progressive alteration, in the natural series from lignite to anthracite.

1.2 This classification is applicable to coals that are composed mainly of vitrinite.

NOTE 1—Coals rich in inertinite or liptinite (exinite), or both, cannot be properly classified because, in those macerals, the properties that determine rank (calorific value, volatile matter, and agglomerating character) differ greatly from those of vitrinite in the same coal. Often such coals can be recognized by megascopic examination. In North America, these coals are mostly nonbanded varieties that contain only a small proportion of vitrain and consist mainly of attrital materials. The degree of metamorphism of nonbanded and other vitrinite-poor coals can be estimated by determining the classification properties of isolated or concentrated vitrinite fractions, or by determining the reflectance of the vitrinite (see Test Method D 2798 and Appendix X1 of this classification). However, in the use of these vitrinite-poor coals, some properties normally associated with rank, such as rheology, combustibility, hardness, and grindability (as well as the rank determining properties) may differ substantially from those of vitrinite-rich coals of the same degree of metamorphism.

The precision of the classification of impure coal may be impaired by the effect of large amounts of mineral matter on the determination of volatile matter and calorific value, and on their calculation to the mineral-matter-free basis.

1.3 The values stated in British thermal units per pound are to be regarded as the standard. The SI equivalents of British thermal units per pound are approximate. All other values in SI units are to be regarded as standard.

2. Referenced Documents

2.1 ASTM Standards:

- D 121 Terminology of Coal and Coke²
- D 720 Test Method for Free-Swelling Index of Coal²
- D 1412 Test Method for Equilibrium Moisture of Coal at 96 to 97 Percent Relative Humidity and 30°C²
- D 1757 Test Method for Sulfur in Ash from Coal and Coke²
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 2234 Practice for Collection of a Gross Sample of Coal²

¹ This classification is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.18 on Classification of Coals.

Current edition approved Sept. 10, 1999. Published January 2000. Originally published as D 388 – 34 T. Last previous edition D 388 – 98a.

² *Annual Book of ASTM Standards*, Vol 05.06.

- D 2798 Test Method for Microscopical Determination of the Reflectance of Vitrinite in a Polished Specimen of Coal²
- D 3172 Practice for Proximate Analysis of Coal and Coke²
- D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke²
- D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal²
- D 3175 Test Method for Volatile Matter in the Analysis Sample of Coal and Coke²
- D 3177 Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke²
- D 3180 Practice for Calculating Coal and Coke Analysis from As-Determined to Different Bases²
- D 3302 Test Method for Total Moisture in Coal²
- D 4596 Practice for Collection of Channel Samples of Coal in the Mine²
- D 5192 Practice for the Collection of Coal Samples from the Core²
- D 5865 Test Method for Gross Calorific Value of Coal and Coke²

3. Terminology

3.1 **Definitions**—For additional definitions of terms used in this classification, refer to Terminology D 121.

3.1.1 **agglomerating**, *adj*—as applied to coal, the property of softening when it is heated to above about 400°C in a nonoxidizing atmosphere, and then appearing as a coherent mass after cooling to room temperature.

3.1.2 **apparent rank**, *n*—of coal, the rank designation assigned to samples other than channel samples or core samples with 100 % recovery, but otherwise conforming to the procedure of Classification D 388.

3.1.3 **coal seam**, *n*—the stratum, layer, or bed of coal that lies between two other rock layers whose compositions differ significantly from that of coal.

3.2 **Abbreviations**—Where it is desired to abbreviate the designation of the ranks of coal, the following abbreviations shall be used:

- ma—meta-anthracite
- an—anthracite
- sa—semianthracite
- lvb—low volatile bituminous
- m vb—medium volatile bituminous
- h vAb—high volatile A bituminous
- h vBb—high volatile B bituminous
- h vCb—high volatile C bituminous

1bA—subbituminous A
 1bB—subbituminous B
 1bC—subbituminous C
 1A—lignite A
 1B—lignite B

Significance and Use

This classification establishes categories of coal based on additional properties that depend principally on the degree of metamorphism to which the coal was subjected while in the ground. These categories indicate ranges of physical and chemical characteristics that are useful in making broad generalizations of the behavior of coal in mining, preparation, and use.

Basis of Classification

Classification is according to fixed carbon and gross calorific value (expressed in British thermal units per pound) related to the mineral-matter-free basis. The higher-rank coals are classified according to fixed carbon on the dry basis; lower-rank coals are classified according to gross calorific value on the moist basis. Agglomerating character is used to differentiate between certain adjacent groups.

Classification by Rank

1 Fixed Carbon and Gross Calorific Value—Coals shall be classified by rank in accordance with Table 1. Classify coals having gross calorific values of 14 000 Btu/lb or more on the dry, mineral-matter-free basis, and coals having fixed carbon 86% or more on the dry, mineral-matter-free basis, according to fixed carbon on the dry, mineral-matter-free basis. Classify coals having gross calorific values less than 14 000 Btu/lb on the moist, mineral-matter-free basis according to gross calorific value on the moist, mineral-matter-free basis, and coals having fixed carbon on the dry, mineral-matter-free basis less than 69%.

2 Agglomerating Character—Classify coals having 86% or more fixed carbon on the dry, mineral-matter-free basis, if agglomerating, in the low volatile group of the bituminous rank. Classify coals having gross calorific values in the range of 10 500 to 11 500 Btu/lb on the moist, mineral-matter-free basis according to their agglomerating character (Table 1).

3 Supplemental Information—A correlation of the ranking of coals by fixed carbon, volatile matter (100—fixed carbon), with the mean minimum reflectance of the vitrinite group macerals in coals determined in one laboratory over a period of several years is shown in Appendix X1.

Sampling

1 Samples—Classify a coal seam, or part of a coal seam, by locality based on the average analysis and gross calorific value (and agglomerating character where required) of not less than three and preferably five or more face channel samples or samples taken in different and uniformly distributed localities, either within the same mine or closely adjacent mines representing a continuous and compact area not greater than approximately four square miles in regions of geological homogeneity. In regions in which conditions indicate that the coal quality varies rapidly in short distances, the spacing of sampling points and grouping of analyses to provide average

values shall not be such that coals of obviously different rank will be used in calculating average values.

7.1.1 Take channel samples by excluding mineral partings more than 1 cm ($\frac{3}{8}$ in.) and lenses or concretions (such as sulfur balls) more than 1.25 cm ($\frac{1}{2}$ in.) thick and 5 cm (2 in.) wide, as specified in Practice D 4596.

7.1.2 A drill core sample may be used provided it was collected as specified in Practice D 5192 and meets the following provisions: core recovery is 100% of the seam, the major mineral partings and concretions are excluded as specified in 7.1.1, and drilling mud is removed from the core (see also 7.1.6).

7.1.3 Place all samples in metal or plastic cans with airtight lids, or heavy vapor impervious bags, properly sealed to preserve inherent moisture.

7.1.4 Analyses of samples from outcrops or from weathered or oxidized coal shall not be used for classification by rank.

7.1.5 In case the coal is likely to be classified on the *moist* basis, that is, inclusive of its natural complement of inherent moisture, take samples in a manner most likely to preserve inherent moisture for purposes of analysis. Because some of the moisture in a freshly collected sample condenses on the inside of the sample container, weigh both the container and the coal before and after air drying, and report the total loss in weight as air-drying loss.

7.1.6 If the sample is a core or if it is impossible to sample the coal without including visible surface moisture, or if there may be other reasons to question the accuracy of inherent moisture content determinable from the sample, and the coal is likely to be classified on the *moist* basis, the sampler shall include the following statement in the description: *Moisture questionable*. Samples so marked shall not be used for classification on a moist basis unless brought to a standard condition of moisture equilibrium at 30°C in a vacuum desiccator containing a saturated solution of potassium sulfate (97% humidity) as specified in Test Method D 1412. Analyses of such samples that have been treated in this manner shall be designated as *samples equilibrated at 30°C and 97% humidity*.

7.2 *Other Types of Samples*—A standard rank determination cannot be made unless samples have been obtained in accordance with 7.1. However, the relation to standard determinations may be usefully given for other types of samples taken under unspecified conditions, providing the same standards of analysis and computation are followed. Designate these comparative indications as *apparent rank*, which indicates the correct relative position for the sample analyzed but does not imply any standards of sampling. Whenever apparent rank is stated, give additional information as to the nature of the sample.

7.2.1 The apparent rank of the coal product from a mine shall be based on representative samples taken in accordance with the Organization and Planning of Sampling Operations section (Section 7) of Practice D 2234.

7.2.2 In case the coal is likely to be classed on the *moist* basis, take samples at the tipple or preparation plant and seal the sample to prevent loss of moisture.

8. Methods of Analysis and Testing

8.1 *Laboratory Sampling and Analysis*—Prepare coal in

accordance with Method D 2013 and analyze it in accordance with Test Methods D 3173, D 3174, D 3175, D 3177, D 3302, and Practice D 3172. Determine its gross calorific value in accordance with Test Method D 5865. Determine the sulfur trioxide (SO₃) retained in the ash in accordance with Test Method D 1757 and express the result on a dry basis. Inherent moisture is reported as as-received moisture if the sample was collected according to 7.1.1 or as equilibrium moisture if 7.1.6 (Test Method D 1412) applies.

8.2 Adjust the ash value determined in accordance with Test Method D 3174 to be free of sulfate as follows:

$$A = A_d \left(1 - \frac{SO_3}{100} \right) \left(1 - \frac{M}{100} \right) \quad (1)$$

where:

- A = adjusted ash value on the inherent moist basis,
- A_d = ash yield, dry basis, determined in accordance with Test Method D 3174,
- SO₃ = in the ash determined in accordance with Test Method D 1757, and
- M = inherent moisture.

Add to the value of fixed carbon that is determined in accordance with Practice D 3172 the value of the SO₃ determined in the ash to obtain the value FC to be used in Eq 2.

8.3 *Agglomerating Character*—The test carried out by the examination of the residue in the platinum crucible incident to the volatile matter determination shall be used.³ Coals which, in the volatile matter determination, produce either an agglomerate button that will support a 500-g weight without pulverizing, or a button showing swelling or cell structure, shall be considered agglomerating from the standpoint of classification. In addition, a result of 1.0 or more on the Free Swelling Index

test (Test Method D 720) may also be used to indicate if it is agglomerating; a result of 0.5 or 0 indicates the coal is nonagglomerating.

9. Calculation to Mineral-Matter-Free Basis

9.1 *Calculation of Fixed Carbon and Calorific Value*—For classification of coal according to rank, calculate fixed carbon and gross calorific value to the mineral-matter-free (Mm) basis in accordance with the Parr formulas,⁴ Eq 2-4. This section contains information concerning the development of the formulas as well as other ranking considerations and examples of the calculations (Table 1) are provided in Appendix 2.

9.2 Calculate to Mm-free basis as follows:

9.2.1 *Parr Formulas*:

$$\text{Dry, Mm-free FC} = 100(\text{FC} - 0.15S) / (100 - (M + 1.08A + 0.5S))$$

$$\text{Dry, Mm-free VM} = 100 - \text{Dry, Mm-free FC}$$

$$\text{Moist, Mm-free Btu} = 100(\text{Btu} - 50S) / (100 - (1.08A + 0.5S))$$

where:

- Btu = gross calorific value, Btu/lb,
- FC = fixed carbon, %,
- VM = volatile matter, %,
- M = moisture, %,
- A = ash, %, and
- S = sulfur, %.

In Eq 2 and Eq 4, the quantities are all on the inherent moisture basis. Fixed carbon (FC) and ash (A) are adjusted to the SO₃-free basis in accordance with 8.2.

10. Keywords

10.1 anthracite; bituminous; coal; lignite; rank

⁴ Parr, S. W., "The Classification of Coal," *Bulletin No. 180*, Engineering Experiment Station, University of Illinois, 1928.

APPENDIXES

(Nonmandatory Information)

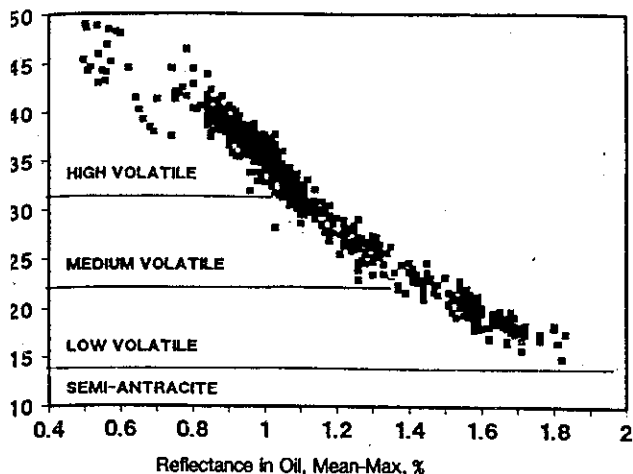
X1. CORRELATION OF VOLATILE MATTER WITH MEAN-MAXIMUM REFLECTANCE OF VITRINITE

X1.1 The reflectance of vitrinite in a sample of coal, as determined by Test Method D 2798, provides a useful guide to the rank of the coal. The correlation of the mean-maximum reflectance of all varieties of vitrinite with volatile matter, expressed on a dry and mineral-matter-free basis, is given in Fig. X1.1. Data are plotted for 807 coal samples that contained less than 8 % ash from many different coal fields in North America. All data were determined by a single laboratory, with several different analysts over a period of several years. The plot shows a range of reflectances for three important rank groups:

| Reflectance Range in Oil, Mean-Max, % | Distribution Midpoints | Rank |
|---------------------------------------|------------------------|------|
| <1.15 | <1.1 | hvb |
| 1.02-1.55 | 1.10-1.45 | mvb |
| 1.35-2.0(?) | 1.45-2.0(?) | lvb |

NOTE X1.1—Coals with the same vitrinite reflectance and similar maceral compositions may have different rheological and fluorescence properties and even burn and carbonize differently. These differences may be due to such diverse factors as their geologic age, environment, and mode of accumulation (time, temperature, and pressure), and differences in the plants that contributed to their formation. Thus, the use of vitrinite reflectance for selecting coals for use may need additional

³ Gilmore, R. E., Connell, G. P., and Nicholls, J. H. H., "Agglomerating and Agglutinating Tests for Classifying Weakly Caking Coals," *Transactions, American Institute of Mining and Metallurgical Engineers, Coal Division*, Vol 108, 1934, p. 255.



X1.1 Relation Between the Rank of U.S. Coals and Vitrinite Reflectance

same reflectance but different fluorescence properties are known to produce different carbon forms that have different physical (strength) and chemical (reactivity) properties.

X1.2 The midpoints given above are the midpoints of the distribution for the lower and upper boundary points on the reflectance scale for the indicated rank. Of the 807 coals, those that contain greater than 25 volume % inertinites tend to plot on the lower side of the distribution range than do the others that contain more vitrinites and liptinites.

ications to predict their utilization potential. This is particularly tant in selecting coals for coke production since vitrinites with the

X2. BACKGROUND INFORMATION ON THE PARR EQUATIONS AND OTHER RANKING CONSIDERATIONS

2.1 Introduction—Coals are ranked according to Classification D 388 on a mineral matter-free basis, dry or moist, depending on the parameter that applies. The rank meters—either volatile matter (or fixed carbon) or gross calorific values—are commonly reported by laboratories on the as-received, dry-and-ash-free basis. These reported values must be converted to the mineral-matter-free basis for ranking purposes. Thus converted, the properties of the maceral (carcinaceous) material are used as ranking criteria, and the effects of variable mineral matter contents, which are unrelated to rank, are eliminated. In essence, only the “pure coal” fraction of the given sample is being ranked. The Parr formula is used to correct for the original mineral matter in the coal by using the ash yield and total sulfur content determined on that coal as follows:

$$Mm = 1.08A + 0.55S$$

where:

A = ash yield (ASTM Test Method D 3174) and
S = total sulfur content (ASTM Test Methods D 3177).

This formula assumes that clay minerals, with an average water of hydration content of 8 %, and pyrite, which contains essentially all the sulfur, are the only mineral groups present. Furthermore, the following reactions are assumed to occur during ashing: (1) the hydroxyl groups from the clay minerals are lost to the atmosphere; (2) the sulfur converts to sulfur dioxide, which also is lost; and (3) pyrite decomposes to iron oxide and iron is retained in the ash. The Parr formula attempts to correct the measured ash and sulfur for these reactions by adjusting their mass back to that of the original minerals in the coal. By using this formula, the varying amounts of mineral matter can be factored out of the ranking of coals. For example, Samples A and B in Table X2.1 are both ranked as Lignite A because they have similar gross calorific values when calculated to a moist, mineral-matter-free basis (gross calorific value_{m,m,m,f}), in contrast to their gross calorific values which are quite different on an as-received basis. In this example, differing mineral contents are thus factored out for the purposes of ranking.

Section X2.3 provides useful equations that enable the

Designation: D 3173 – 00

Standard Test Method for Moisture in the Analysis Sample of Coal and Coke¹

This standard is issued under the fixed designation D 3173; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

This test method covers the determination of moisture in analysis sample of coal or coke. It is used for calculating analytical results to a dry basis. When used in conjunction with the air drying loss as determined in accordance with D 2013 or Practice D 346, each analytical result can be reduced to an as-received basis:

This standard does not purport to address all of the concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

Referenced Documents

STM Standards:

- D 346 Practice for Collection and Preparation of Coke Samples for Laboratory Analysis²
- D 2013 Method of Preparing Coal Samples for Analysis²
- D 3180 Practice for Calculating Coal and Coke Analyses on As-Determined to Different Bases²
- D 3173 Test Method for Total Moisture in Coal²

Summary of Test Method

Moisture is determined by establishing the loss in weight of the sample when heated under rigidly controlled conditions of temperature, time and atmosphere, sample and equipment specifications.

Significance and Use

Moisture as determined by this test method is used for reporting other analytical results to a moisture free basis. Procedures in Practice D 3180. Moisture percent determined by this test method may be used in conjunction with the moisture loss determined in Method D 2013 and Test Method D 3302 to determine total moisture in coal. Total moisture is used for calculating other analytical results to "as received" basis using Practice D 3180. Moisture, ash, volatile matter and fixed carbon percents constitute the proximate analysis of coal and coke.

¹ This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of

² This edition approved Nov. 10, 2000. Published January 2001. Originally published as D 3173 – 73. Last previous edition D 3173 – 87 (1996).

³ Annual Book of ASTM Standards, Vol 05.05.

5. Analysis Sample

5.1 The analysis sample is that sample which has been pulverized to pass 250- μ m (No. 60) sieve as prepared in accordance with Practice D 346 or Method D 2013.

6. Apparatus

6.1 Drying Oven, for coal samples:

6.1.1 For determining the moisture of coal, the oven shall be so constructed as to have a uniform temperature in all parts, have a minimum of air space, and be capable of temperature regulation between the limits of 104 and 110°C. It may be of the form shown in Fig. 1. Provision shall be made for renewing the preheated air in the oven at the rate of two to four times a minute, with the air dried as defined in 7.1.

6.1.2 In the oven shown in Fig. 1, the door should contain a hole of approximately 1/8 in. (3.2 mm) in diameter near the bottom to permit a free flow of air through the oven space.

6.2 Drying Oven, for coke samples. For determining the moisture of coke, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation between limits of 104 and 110°C may be used.

6.3 Capsules, with covers. A convenient form, which allows the ash determination to be made on the same sample, is a porcelain capsule, 7/8 in. (22 mm) in depth and 1 3/4 in. (44 mm) in diameter, or a fused silica capsule of similar shape. These capsules shall be used with a well-fitting flat aluminum cover, illustrated in Fig. 2. Platinum crucibles or glass capsules with ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

7. Reagents

7.1 Dry Air—Air used to purge the drying oven should be dried to a moisture content of 1.9 mg/L or less. (Dew point – 10°C or less.) Any desiccant or drying method capable of achieving this degree of dryness is suitable.

7.2 Desiccants—Materials suitable for use in the desiccator may be chosen from the following:

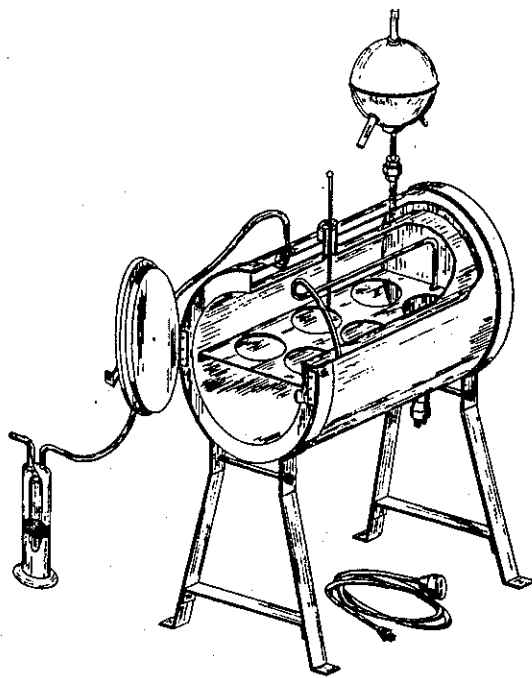
7.2.1 Anhydrous Calcium Sulfate (0.004 mg/L).

7.2.2 Silica Gel.

7.2.3 Magnesium Perchlorate (0.0005 mg/L).

7.2.4 Sulfuric Acid, Concentrated (0.003 mg/L).

7.2.5 The desiccant must be kept fresh enough to assure that the air in the desiccator is dry as defined in 7.1. Values in parentheses () are literature values for the residual amount of moisture in air at equilibrium with these desiccants. (Warning:



NOTE 1—Details in U.S. Bureau of Mines Bulletin No. 492, 1951, p 6.
FIG. 1 Moisture Oven

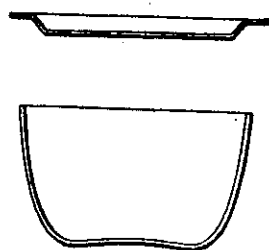


FIG. 2 Capsule for Use in Determining Moisture

Sulfuric acid is corrosive and can cause severe damage to eyes, skin, and clothing. Magnesium perchlorate is a strong oxidant and can react violently with organic materials.)

8. Procedure for Sample Passing a 250- μ m (No. 60) Sieve

8.1 Heat the empty capsules under the conditions at which the sample is to be dried, place the stopper or cover on the capsule, cool over a desiccant for 15 to 30 min, and weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g of the sample. Put this quickly into the capsule, close, and weigh at once to the nearest ± 0.1 mg.

8.2 An alternative procedure for weighing the sample (more subject to error) is as follows: After transferring an amount of the sample slightly in excess of 1 g, bring to exactly 1 g in weight (± 0.5 mg) by quickly removing the excess weight of the sample with a spatula. The utmost dispatch must be used to minimize the exposure of the sample until the weight is determined.

8.3 After removing the covers, quickly place the capsules in a preheated oven (at 104 to 110°C) through which passes a

current of dry air. (The current of dry air is not necessary for coke.) Close the oven at once and heat for 1 h. Open the cover the capsules quickly, cool in a desiccator over desiccant, and weigh as soon as the capsules have reached room temperature.

8.4 Use the percentage of moisture in the sample passing a 250- μ m (No. 60) sieve to calculate the results of the analyses to a dry basis.

9. Calculations

9.1 Calculate the percent moisture in the analysis sample as follows:

$$\text{Moisture in analysis sample, \%} = [(A - B)/A] \times 100$$

where:

- A = grams of sample used and
- B = grams of sample after heating.

10. Precision and Bias

10.1 *Precision*—The precision of this method for the determination of residual moisture in the analysis sample of coke is shown in Table 1. The precision characterized by repeatability (S_r , r) and reproducibility (S_R , R) is described in Table A1.1 in Annex A1.

10.1.1 *Repeatability Limit (r)*—The value below which the absolute difference between two test results of separate consecutive test determinations, carried out on the same sample in the same laboratory by the same operator using the same apparatus on samples taken at random from a single quantity of homogenous material, may be expected to occur with a probability of approximately 95 %.

10.1.2 *Reproducibility Limit (R)*—The value below which the absolute difference between two test results, carried out in different laboratories using samples taken at random from a single quantity of material that is as nearly homogenous as possible, may be expected to occur with a probability of approximately 95 %.

10.2 *Bias*—Certified Reference Materials are not available for the determination of bias by this test method.

10.3 An interlaboratory study, designed consistent with Practice E 691, was conducted in 1995. Twelve labs participated. The details of the study and supporting data are given in ASTM Research Report D05-1020 filed at ASTM Headquarters (see Note 1).

NOTE 1—One coke sample was analyzed in the interlaboratory study. The average moisture of the coke sample was 0.36 %. The repeatability limit for this sample is 0.10. The reproducibility limit for this sample is 0.15. The repeatability standard deviation for this sample is 0.036. The reproducibility standard deviation for this sample is 0.053.

TABLE 1 Precision

| Range | Repeatability Limit (r) | Reproducibility Limit (R) |
|--------------|-----------------------------|-------------------------------|
| 1.0 - 21.9 % | $0.09 + 0.01\bar{x}^A$ | $0.23 + 0.02\bar{x}^A$ |

^AWhere \bar{x} is the average of two single test results.

 D 3173

ANNEX

(Mandatory Information)

A1. PRECISION STATISTICS

1.1 The precision of this test method, characterized by repeatability (S_r , r) and reproducibility (S_R , R) has been determined for the following materials as listed in Table A1.1.

1.2 *Repeatability Standard Deviation* (S_r)—The standard

deviation of test results obtained under repeatability conditions.

A1.3 *Reproducibility Standard Deviation* (S_R)—The standard deviation of test results obtained under reproducibility conditions.

TABLE A1.1 Repeatability (S_r , r) and Reproducibility (S_R , R) Parameters Used for Calculation of Precision Statement

| Material | Average | S_r | S_R | r | R |
|----------|---------|--------|--------|--------|--------|
| lvb | 0.9683 | 0.0479 | 0.0853 | 0.1341 | 0.2388 |
| hvAb | 1.5689 | 0.0569 | 0.1387 | 0.1593 | 0.3884 |
| hvAb | 3.1178 | 0.0559 | 0.0977 | 0.1564 | 0.2736 |
| hvCb | 5.4428 | 0.0601 | 0.1408 | 0.1682 | 0.3943 |
| hvCb | 9.6392 | 0.0636 | 0.1004 | 0.1781 | 0.2811 |
| subB | 11.9 | 0.1252 | 0.2193 | 0.3505 | 0.614 |
| subA | 12.4556 | 0.0798 | 0.1188 | 0.2234 | 0.3326 |
| subA | 15.1753 | 0.0577 | 0.1737 | 0.1615 | 0.4865 |
| subC | 21.9461 | 0.1949 | 0.2843 | 0.5456 | 0.796 |

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Designation: D 3683 – 94 (Reapproved 2000)

Standard Test Method for Trace Elements in Coal and Coke Ash by Atomic Absorption¹

This standard is issued under the fixed designation D 3683; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method² describes a procedure for the determination of beryllium, chromium, copper, manganese, nickel, lead, vanadium, and zinc in coal ash or coke ash.

NOTE 1—Although not included, this test method can be applicable to the determination of other trace elements, for example, cadmium.

1.2 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

1.3 The values stated in SI units (IEEE/ASTM SI 10) should be regarded as the standard.

2. Referenced Documents

2.1 ASTM Standards:

D 346 Practice for Collection and Preparation of Coke Samples For Laboratory Analysis³

D 1193 Specification for Reagent Water⁴

D 2013 Method of Preparing Coal Samples for Analysis³

D 3173 Test Method for Moisture in the Analysis Sample of Coal and Coke³

D 3180 Practice for Calculating Coal and Coke Analyses from As-Determined to Different Bases³

D 5142 Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures³

IEEE/ASTM SI 10 Standard for Use of the International System of Units (SI): The Modern Metric System⁵

NOTE 2—Method D 2013 specifies coal ground to pass through a 60-mesh (250- μ m) screen. For the trace element determinations in this test method—100-mesh (150- μ m) coal is recommended.

3. Summary of Test Method

3.1 Coal or coke is ashed, the ash is dissolved by mineral acids, and the individual elements determined by atomic absorption spectrometry.

4. Significance and Use

4.1 Many trace elements occur in coal, primarily as a part of the mineral matter but may also be associated with the organic matrix. Concern over release of certain trace elements to the environment as a result of coal utilization has made the determination of these elements an increasingly important aspect of coal analysis.

4.2 When coal ash is prepared in accordance with this method, the eight elements listed in 1.1 are quantitatively retained in the ash and are representative of concentrations in the coal. Concentrations of these and other elements in power plant ash, industrial process ash, fly ash, and so forth, may not be representative of total quantities in the coal.

5. Apparatus

5.1 *Atomic Absorption Spectrometer*—Any dual-channel instrument using a deuterium (D_2) arc background corrector or other comparable simultaneous background correction system.

5.2 *Muffle Furnace*, with temperature control.

5.3 *Bottles*, polyethylene or polytetrafluoroethylene, 125-mL capacity, with screw-cap lids, capable of withstanding temperatures up to 130°C.

5.4 *Volumetric Flasks*, 100-mL capacity.

5.5 *Steam Bath*.

5.6 *Analytical Balance*, capable of weighing to 0.1 mg.

5.7 *Crucibles*, 50-mL quartz or high silica.

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.⁶ Other grades may

¹ This test method is under the jurisdiction of ASTM Committee D05 on Coal and Coke, and is the direct responsibility of Subcommittee D05.29 on Major Elements in Ash and Trace Elements in Coal.

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² For information concerning experimental work on which this test method is based, see Bernas, B., "A New Method for the Decomposition and Comprehensive Analysis of Silicates by Atomic Absorption Spectrometry," *Analytical Chemistry*, ANCHA, Vol. 40, 1968, pp. 1682–86.

³ *Annual Book of ASTM Standards*, Vol. 05.06.

⁴ *Annual Book of ASTM Standards*, Vol. 11.01.

⁵ *Annual Book of ASTM Standards*, Vol. 14.04.

⁶ *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopoeia and National Formulary*, U.S. Pharmacopoeial Convention, Inc. (USPC), Rockville, MD.

using the same apparatus, should not exceed the repeatability limits for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the repeatability limit, there is reason to question one, or both, of the test results. The repeatability limits determined by this method are listed in Table 2.

TABLE 2 Repeatability

| Element | Air-Dried Coal, ppm (µg/g) | |
|---------|----------------------------|--------------------|
| | Repeatability ^A | Range ^B |
| Be | 0.2 | 0.5 to 5 |
| Cr | 3 | 5 to 50 |
| Cu | 2 | 5 to 50 |
| Mn | 3 | 10 to 300 |
| Ni | 1 | <5 |
| Ni | 3 | 5 to 30 |
| Pb | 2 | 10 to 100 |
| V | 5 | 10 to 100 |
| Zn | 3 | <50 |
| Zn | 8 | 50 to 100 |

^AValues should be considered as a general guide for the kinds of repeatability and reproducibility obtainable and not necessarily as values from which no deviation is permissible.

^BApproximate range of concentrations within which sample results used for statistical evaluation fall.

11.1.2 *Reproducibility*—The difference in absolute value of replicate determinations carried out in different laboratories, on representative samples prepared from the same bulk sample after the last stage of reduction, should not exceed the reproducibility limit for more than 5 % of such paired values (95 % confidence level). When such a difference is found to exceed the reproducibility limit, there is reason to question one,

or both, of the test results. The reproducibility limits mined by this test method are listed in Table 3.

11.2 *Bias*—Standard Reference Material 1632, a Ni Institute of Standards and Technology (NIST) certified sample, was analyzed with the results which are tabulated in Table 4.

NOTE 11—The NIST value for beryllium is not certified and is given for informational purposes only. Values for Test Method D 3683 represent the mean of the means from four separate laboratories, each of which performed four replicate analyses on four separate samples of the coal standard.

12. Keywords

12.1 coal; coal ash; coke ash; trace elements; atomic absorption spectroscopy

TABLE 3 Reproducibility

| Element | Air-Dried Coal, ppm (µg/g) | |
|---------|------------------------------|--------------------|
| | Reproducibility ^A | Range ^B |
| Be | 0.5 | 0.5 to 5 |
| Cr | 5 | 5 to 50 |
| Cu | 3 | 5 to 50 |
| Mn | 6 | <50 |
| Mn | 20 | 50 to 500 |
| Ni | 3 | <5 |
| Ni | 9 | 9 to 30 |
| Pb | 9 | 10 to 100 |
| V | 9 | 10 to 50 |
| V | 20 | 50 to 100 |
| Zn | 4 | <50 |
| Zn | 17 | 50 to 100 |

^AValues should be considered as a general guide for the kinds of repeatability and reproducibility obtainable and not necessarily as values from which no deviation is permissible.

^BApproximate range of concentrations within which sample results used for statistical evaluation fall.


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TABLE 4 Bias

| 32 | Air-Dried Coal, ppm ($\mu\text{g/g}$) | | | | | | | |
|----|---|----------------|----------------|--------------|--------------|--------------|--------------|------------|
| | Be | Cr | Cu | Mn | Ni | Pb | V | Zn |
| | 1.5 ^A | 20.2 \pm 0.5 | 18.2 \pm 2 | 40 \pm 3 | 15 \pm 1 | 30 \pm 9 | 35 \pm 3 | 37 \pm 4 |
| | 1.5 \pm 0.1 | 20.0 \pm 1 | 17.4 \pm 0.6 | 43.8 \pm 3 | 14.6 \pm 3 | 27.8 \pm 4 | 45.7 \pm 4 | 37 \pm 4 |

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