

## Sequestration of Carbon Dioxide in Coal Seams

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### Introduction

The sequestration of CO<sub>2</sub> in coal seams is seen as a possible way to mitigate the rising atmospheric concentrations of CO<sub>2</sub> (Reichle et al. 1999). Technologies that have been developed for enhanced oil recovery and enhanced coal bed methane recovery could be applied to the long-term disposal of CO<sub>2</sub>. In order to determine which, if any, coal seams would be good disposal sites and under what environmental conditions the sequestered CO<sub>2</sub> would remain stable, a better understanding is needed of the chemistry of the coal-CO<sub>2</sub> (or combustion gas) system(s). Among the R&D priorities for coal seam sequestration listed in the Reichle report are: adsorption/desorption of CO<sub>2</sub>, interaction with SO<sub>x</sub> and NO<sub>x</sub> and coal swelling behavior caused by CO<sub>2</sub> adsorption (Reichle et al. 1999). Studies in these and related areas will help define the CO<sub>2</sub> trapping mechanisms.

One of the earliest studies of the adsorption of CO<sub>2</sub> on coal used the BET equation to calculate the CO<sub>2</sub> surface areas of anthracites (Walker and Geller 1956). That the diffusion of CO<sub>2</sub> through coals of various ranks is an activated process was established not long afterward (Nandi and Walker 1965). Despite of the fact that these, and many studies since then, have been performed at low pressure and often at low temperature in order to investigate the surface area of the coal (Mahajan 1991, and references therein), they have provided information which is relevant to today's sequestration projects. The large CO<sub>2</sub> adsorption capacities of coals and the CO<sub>2</sub>-induced swelling of coals are two properties that were documented early (Mahajan 1991). The adsorption of CO<sub>2</sub> and other gases, especially methane, has also been studied in efforts to increase the safety of coal mining. In this regard, it has long been recognized that, although the gas in coal seams can exist as free gas in cracks and fractures, most of the gas in coal is adsorbed on the internal surface of the micropores (Kim and Kissell 1986). More recently, CO<sub>2</sub> adsorption on coal has been studied as a means of enhancing the gas production in coal bed methane recovery projects. Amoco has studied the adsorption of nitrogen, methane, carbon dioxide, and their mixtures to provide data for the modeling of gas recovery from coal bed methane reservoirs (Chaback et al. 1996, DeGance et al. 1993). Burlington Resources, the largest producer of coal-bed methane, has been injecting CO<sub>2</sub> to enhance methane production since 1996 (Stevens et al. 1998). Thus, there is at

present a large body of scientific studies and practical information to lend credence to the coal-seam sequestration scenario.

## **The Problem**

The extent to which coal can adsorb CO<sub>2</sub> 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 effect of both physical and chemical changes need to be understood. Parameters such as temperature, pressure, and pH might be expected to have a moderate to large influence; salinity might be expected to be less important.

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 CO<sub>2</sub> via surface adsorption, pore filling, and solid solution (Larsen et al. 1995). 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.

In the absence of external influences, underground temperatures tend to be constant over time but increase with depth. The adsorption of CO<sub>2</sub> is exothermic (Starzewski and Grillet 1989) and will provide a heat source, at least during the active pumping phase of sequestration. Also, some sequestration scenarios would provide additional heating mechanisms such as by the dissolution of co-sequestered acidic gases (SO<sub>x</sub>, NO<sub>x</sub>) or by reaction with residual oxygen in the combustion gas. Thus, it is important to know how temperature will affect the CO<sub>2</sub> adsorption onto the coal and whether the magnitude of this effect is universal for all coals or is rank or maceral dependent.

Even if initially dry, the seam will certainly 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 minerals with which it is in contact. In natural systems, pH is often an important parameter (Stumm and Morgan 1996) and it will change during sequestration. Because of the formation of carbonic acid, the pH within the sequestration media will drop to around 3 at high CO<sub>2</sub> pressures, favoring the dissolution of calcite. This may be beneficial if mineral dissolution provides better access to the organic matrix, but would be detrimental if dissolution of cap-rock resulted. The effect of the sequestration on pH would be more dramatic for those scenarios in which the SO<sub>x</sub> and NO<sub>x</sub> were not removed by prior separation and are sequestered along with the CO<sub>2</sub>. Little is known about the potential effect of such a pH change on the ability of the organic matrix to adsorb CO<sub>2</sub>. It is well recognized that adsorption of on solid surfaces is affected by the pH of the surrounding media (Stumm and Morgan 1996). Solids in contact with solutions with a pH above their isoelectric point acquire a net negative surface charge; those in contact with solutions with a pH below their isoelectric point acquire a net positive surface charge. The extent to which pH changes will affect the CO<sub>2</sub> adsorption capacity of coals has not been investigated.

Depending on the capture technology, the CO<sub>2</sub> stream may be nearly pure CO<sub>2</sub>, 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 (Kim and Kissell 1986) and act to inhibit or enhance the CO<sub>2</sub> sequestration. In the case of a gassy coal seam, it may be advantageous to displace and capture the

methane as a profit-making part of the operation. This displacement may be enhanced by secondary combustion gases in the  $\text{CO}_2$  such as  $\text{SO}_x$  and  $\text{NO}_x$ .

The composition of the post sequestration gas and liquid phases may change with time. Even slow reactions can become important over geologic-sequestration time scales. Also, microbes have an uncanny ability to adapt to many environments and are known to populate even deep geologic strata, at least to 9000 feet below the surface (Amy and Haldeman 1997). Under oxic conditions, gases such as  $\text{SO}_x$ ,  $\text{NO}_x$ , and  $\text{CO}$  may be produced either chemically or biologically. Under anoxic conditions, methane and  $\text{H}_2\text{S}$  may be produced by anaerobic microbes. These gases may displace  $\text{CO}_2$  and thus limit the durability of the sequestration.

Knowledge of the extent to which coals can adsorb  $\text{CO}_2$  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.

## **Approach**

In this paper, the interaction of one of the Argonne Premium Coal Samples with  $\text{CO}_2$  is studied under a variety of conditions. Argonne samples, which include a representative sample of every rank, are among the most widely studied coals in the world. Because of this, there exists a vast database of measurements and studies which can aid in the interpretation of results (Vorres 1993). Our approach is to investigate the effect of various parameters such as pressure, temperature, pH, and salinity on the adsorption isotherms of these coals. Herein, the effects of temperature, pressure, and pH on the  $\text{CO}_2$  adsorption capacity of one of these samples, the Upper Freeport coal, are described.

## **Project Description**

Gas-phase carbon dioxide adsorption isotherms were obtained using a manometric technique (Nodzinski 1998). In the set of experiments described here, the temperature and pressure were maintained at values below the critical temperature and pressure of carbon dioxide, and the temperature was held above the condensation temperature, thereby maintaining gas-phase conditions.

The manometric apparatus consists of a reference cell of known volume from which all gas transfers were made, and a sample cell, also of known volume. The reference cell, contained within a temperature-controlled bath ( $\pm 0.1$  °C), was pressurized to the desired level as indicated on a pressure transducer. The maximum pressure for any given isotherm was limited by the operating temperature and the condensation pressure of carbon dioxide at that temperature. A sample cell of known void volume, which was also placed within the same bath, 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. Similarly, the number of gas-phase moles in the sample cell after the gas transfer was calculated from the post-transfer sample-cell pressure. The missing moles of gas were accounted to the adsorption of  $\text{CO}_2$  onto (into) the coal. The reference cell was then pressurized to a higher pressure and the process was repeated. The individual incremental gas adsorption values ( $dn$ ) were summed to generate the adsorption isotherm in a step-wise fashion. The adsorption isotherm for a given

temperature was plotted as the total number of millimoles of carbon dioxide adsorbed per gram of coal (y-axis) versus the equilibrium sample-cell pressure (x-axis). This method of isotherm construction is shown graphically in Figure 1. The incremental number of moles adsorbed for each pressure change (dn) are shown as the triangles. These increments slowly decrease as higher pressures are attained. The total moles adsorbed (n) are obtained by summing the individual increments and are shown as the circles in Figure 1.

In the experiments investigating the effect of temperature, after completing the experiment at one temperature, the sample was depressurized and evacuated overnight at 22°C. The temperature of the bath was then raised and the process was repeated. From the temperature dependence of the adsorption isotherms, the isosteric heat of adsorption,  $Q_{\text{isosteric}}$ , was calculated from the modified Clausius-Clapeyron equation (Daniels et al. 1962).

$$\ln (P_2/P_1) = Q_{\text{isosteric}} (T_2-T_1) / RT_1T_2$$

Because coals rapidly and irreversibly adsorb atmospheric oxygen (Schmidt 1945), efforts were devoted to maintaining an oxygen-free environment. The precautions taken during the collection, processing and packaging of the Argonne samples (Vorres 1993) and our efforts to maintain an oxygen-free environment ensured that the measured coal properties reflect the activity of the virgin coal as closely as possible under laboratory conditions. Vials of the Argonne Premium coal were opened in accordance with the provided mixing instructions. Vials were opened and all operations were performed in an inert-gas flushed glove bag under a positive pressure of nitrogen gas. Aqueous solutions, when used, were prepared from de-ionized water which had been sparged with and stored under inert gas to remove dissolved oxygen. Coal samples were removed from the glove bag only after they had been placed in the sample cell and capped.

The effect of pH was investigated by pre-treating the coal in aqueous slurries to pH values of 2.4, 6.2, and 12. All procedures were performed in a nitrogen-flushed glove bag. The pH value of 2.4 was achieved by the slow addition of 3.1mM  $H_2SO_4$  to the coal-water slurry. The pH of 12 was achieved in a similar fashion using 10 mM NaOH. The value of 6.2 represents the solution pH resulting from the simple mixing of only the coal and water. The coals were filtered and dried overnight in a vacuum oven at 60°C prior to being loaded into the sample cells.

## Results

### *Effect of Temperature*

The temperature dependence of the carbon dioxide adsorption isotherms for the Argonne Premium Upper Freeport Coal is shown in Figure 2. The isotherms obtained for the three lower temperatures were self-consistent and the entire range of data is plotted. At the highest temperature (55°C), the extent of adsorption at pressures above 300 psia continued to increase linearly and, at 700 psia, had surpassed the extent of adsorption observed at the lower temperatures. While this may indicate a physical change in the coal at the highest temperature, the reproducibility of this result needs to be confirmed and so this portion

of the isotherm is not depicted in Figure 2. Within the pressure-temperature range shown in Figure 2, the carbon dioxide adsorption isotherms appear to be non-Langmuir. They fail to approach a limiting value at high pressures as would be predicted by the Langmuir equation. Instead, the amount of carbon dioxide adsorbed becomes nearly linear in the higher pressure region. It should be mentioned that the critical temperature and pressure of carbon dioxide are about 31°C and 1070 psia, respectively (Weast 1979). At temperatures below the critical temperature, increasing pressure will ultimately result in condensation of the carbon dioxide and the apparent amount of “adsorbed” CO<sub>2</sub> would rapidly increase. At temperatures and pressures above the critical point, CO<sub>2</sub> exists as a supercritical fluid. The conditions of the experiments depicted in Figure 2, lie in the gas phase region of the CO<sub>2</sub> phase diagram.

The incremental amount of carbon dioxide that can be adsorbed by the coal drops off dramatically at higher pressures. For example, the amount of carbon dioxide adsorbed during the application of the first 100 psi of CO<sub>2</sub> pressure (0-100 psia) amounts to 0.6 to 0.9 mmole per gram of coal, depending on the temperature. However, the additional amount of CO<sub>2</sub> adsorbed during the addition of the last 100 psi of CO<sub>2</sub> pressure (600-700 psi) amounts to less than an additional 0.1 mmole per gram. From a practical stand-point, this means that disproportionately higher pumping costs per pound of CO<sub>2</sub> will be incurred at higher sequestration pressures.

In the pressure-temperature region studied, the CO<sub>2</sub> capacity of the coal did not exceed 1.4 mmole CO<sub>2</sub>/g coal. This adsorption value corresponds to a CO<sub>2</sub> storage density of about 85 kg CO<sub>2</sub>/m<sup>3</sup> coal. For comparison, the density of liquid phase CO<sub>2</sub> is 600 kg/m<sup>3</sup> (at 30°C).

The effect of increasing temperature is to decrease the equilibrium adsorption capacity of the coal. This is expected because higher temperatures increasingly favor the gas-phase due to the T<sup>a</sup>S entropy term in the free energy expression. This means that otherwise equivalent, but deeper, warmer seams will adsorb less CO<sub>2</sub> at a given pressure than shallower, cooler ones.

The average isosteric heat of adsorption was calculated to be  $4.85 \pm 0.26$  kcal per mole of CO<sub>2</sub> adsorbed ( $20.3 \pm 1.1$  kJ/mole). This is higher than the heat of vaporization of CO<sub>2</sub> in this temperature range which is only about 1.3 kcal/mol, even at the lowest temperature. However, this value is lower than the 12 kcal/mol (50 kJ/mol) value measured via calorimetry, albeit at very low coverage (Starzewski and Grillet, 1989). Nodzinski (1998) found a range from 6 to 14 kcal/mol (26-59 kJ/mol) for a selection of hard coals. Coal contains a wide variety of adsorption sites. Thermodynamics would suggest that the most active sites would be occupied first and provide the greatest heat of adsorption. Thus, it is to be expected that the heat evolved per mole of CO<sub>2</sub> at low coverage would be higher than the heat evolved at high coverage. We find that the strength of the average, high-coverage, interaction is about the same as for a hydrogen bond, about 5 kcal/mol. This is in qualitative agreement with results that have related the CO<sub>2</sub> adsorption capacity to oxygen functionality (Nishino 2001). Thus, it appears that the binding energy found here falls between simple condensation and the higher energy adsorption onto the more active sites.

The change in the heat of adsorption with increasing extent of adsorption is shown in Figure 3. The slight drift to higher heat values at coverages below 1 mmole/gram amounts to less than ½ kcal/mole. This may reflect small changes resulting from fresh adsorption sites being made available during coal swelling. Coals swell upon exposure to CO<sub>2</sub> and the extent of expansion increases with increasing CO<sub>2</sub> pressure (Reucroft and Patel 1986, Reucroft and Sethuraman 1987). However, the application of an external load limits the extent of coal swelling (Walker et al. 1988) so its practical influence on coal-seam sequestration may be limited by the over-burden pressure. The sharp decrease in the heat of adsorption at coverages above 1.2 mmole/gram may be due to the saturation of more reactive adsorption sites on the coal.

## *Effect of pH*

The effect of pH on the chemistry of aqueous CO<sub>2</sub> is well known (Stumm and Morgan 1996). At a pH of 9, dissolved CO<sub>2</sub> exists as the carbonate ion and mineral carbonates are stable. At a pH of 2, mineral carbonates dissolve, the CO<sub>2</sub> that can remain dissolved exists as H<sub>2</sub>CO<sub>3</sub> and CO<sub>2(aq)</sub> and CO<sub>2(gas)</sub> 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 the higher pH value, the carbonaceous surface, being in an environment above its isoelectric point, assumes a net negative charge. At the lower pH value, the carbonaceous surface assumes a net positive charge. While a pH of 9 will favor, and a pH of 2 disfavor, the aqueous capture of CO<sub>2</sub>, the effect of being above, or below, the carbonaceous isoelectric point is not so obvious. An example of the importance of aqueous parameters to coal-gas interactions can be seen in the case of the coal floatation process where not only pH but also salinity is important for bubble attachment (Li and Somasundaran 1993). Because of the potential importance of pH, we have studied its effect on the ability of the organic matrix to adsorb CO<sub>2</sub> in the absence of the aqueous phase as a confounding factor.

The effect of the coal surface pH was investigated by pre-soaking the coal using aqueous slurries at pH values of 2.4, 6.2, and 12. The coals were filtered and dried overnight in a vacuum oven at 60°C prior to being loaded into the sample cells. These three samples were then compared to each other and to an untreated aliquot of the same coal which had not been oven dried. The effect of these treatments on the CO<sub>2</sub> adsorption capacity of the coal is shown in Figure 4. Note that the coal weights have been adjusted to a dry, ash-free (daf) basis to account for the different levels of mineral matter and moisture in the original sample and these laboratory-generated samples.

The major difference observed is the lower extent of adsorption for those samples that were treated, regardless of treatment. Because these samples were all oven dried whereas the virgin sample was not, the assumption that such mild drying would not affect the results may not be valid. Moisture removal is known to affect the porosity and transport properties of coals, especially lignite and subbituminous coals, but the effects are usually mild for higher rank coals when the drying temperature is below 100°C (Suuberg et al. 1993). Yet, this trend is opposite to that found for the methane adsorption capacity which increased when the moisture was removed from the coal pores by drying (Joubert et al. 1974). Because of the uncertain effect of the drying, it is reasonable to limit the discussion of pH effects to the three treated samples.

As seen in Figure 4, both acid treatment to a pH of 2.4 and a base treatment to a pH of 12 result in an increase in adsorption capacity compared to the coal treated with only de-ionized water. The Upper Freeport coal has a low-temperature ash content of 15%, which includes acid soluble minerals such as calcite (Vorres 1993). The proximate analysis of the acid-washed coal showed an ash reduction from 13.0% to 11.8%. If removal of acid-soluble minerals resulted in increased accessible pore volume, then increased CO<sub>2</sub> capacity would be expected. The ash content of the base treated coal was reduced by only 0.2%. 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 CO<sub>2</sub> to form carbonates. Whatever the mechanism, the acid treatment appears to have a greater effect than the base or neutral treatments in these initial experiments.

## Application

Adsorption isotherms and related information are needed for effective CO<sub>2</sub> sequestration modeling. For example, parameters such as the heat and rate of CO<sub>2</sub> adsorption, the heat capacities of the coal seam components, and the thermal conductivity of the surrounding media must be known or estimated in order to calculate coal-bed temperature rises for various pumping scenarios. As shown in this work (Figure 2), the temperature dependence of the adsorption isotherms can seriously affect the sequestration capacity. Incompletely filled coal seams, or time wasted while waiting for a seam to cool, eventually affects the cost of the sequestration. Similarly, the estimated cost of alternative sequestration scenarios, such as co-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.

## Future Activities

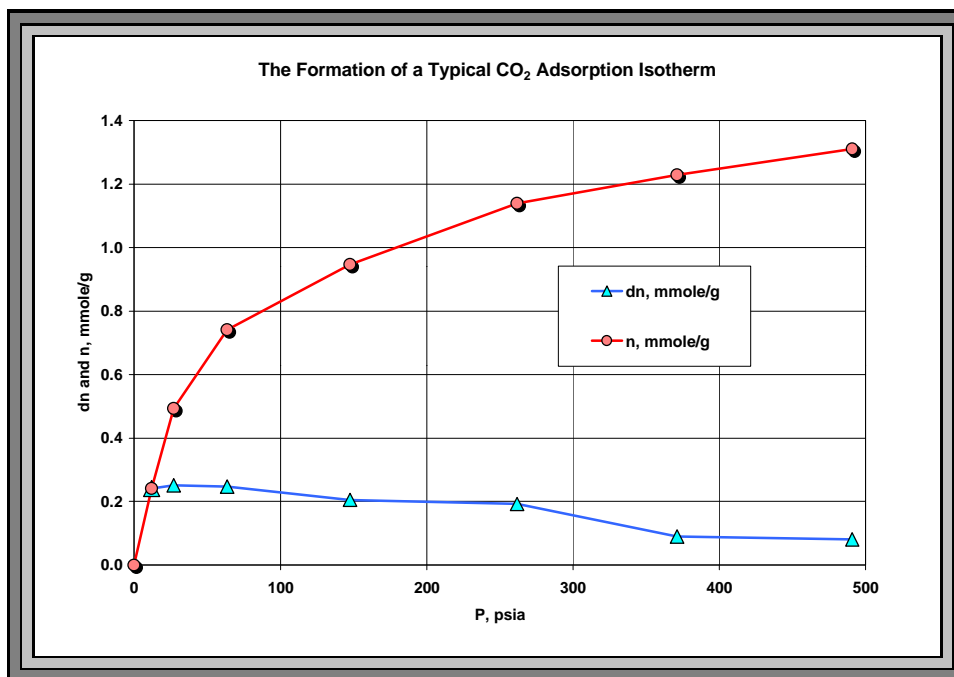
In addition to completing the experiments discussed above, a task devoted to the study of these interactions using techniques adopted from inverse chromatography (IC) will be pursued. One of the major advantages of IC is the ability to generate the entire adsorption and desorption isotherm from a single experiment. The application of IC to physicochemical research is well established (Paryjczak 1975) and has been implemented in both gas chromatography (GC) and high pressure liquid chromatography (HPLC). Here, we will be employing conditions appropriate to supercritical fluid chromatography (SFC) as well. In the IC experiment, properties of the solid, stationary phase are investigated using known solutes (probes), as opposed to the typical chromatography experiment in which a known stationary phase is used to study an unknown gas mixture. Techniques including frontal analysis, displacement chromatography, elution-on-a-plateau, thermo-desorption, and pulse injection can be used to obtain physicochemical measurements such as the extent of irreversible adsorption, adsorption isotherms, and energies of interactions. Some techniques, such as those that require linear chromatography conditions, may not be possible under the conditions we wish to explore for geologic sequestration, whereas others, such as elution-on-a-plateau, seem directly applicable.

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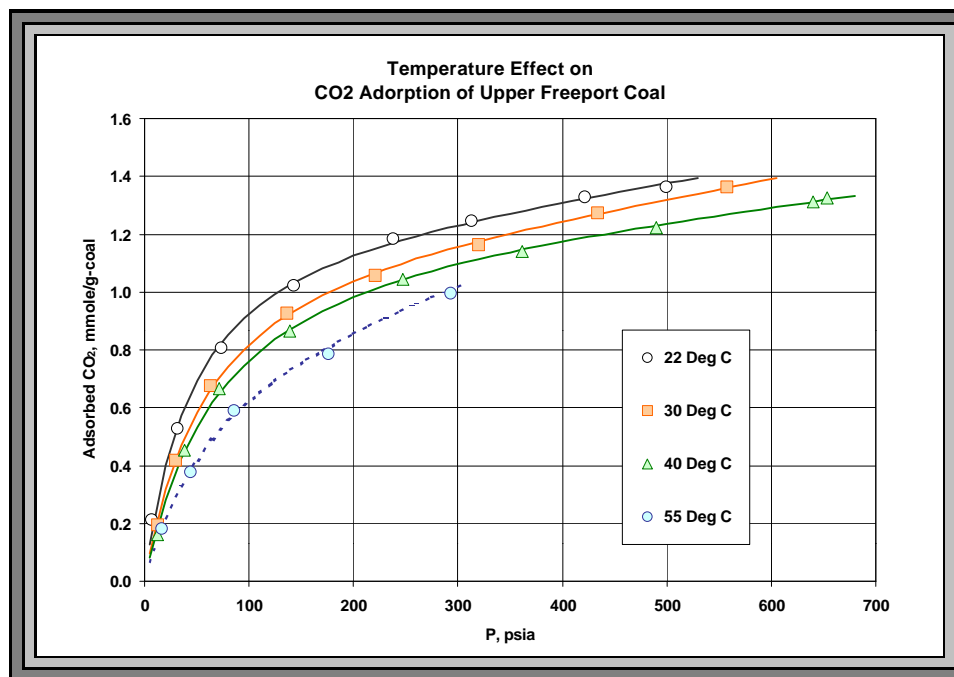
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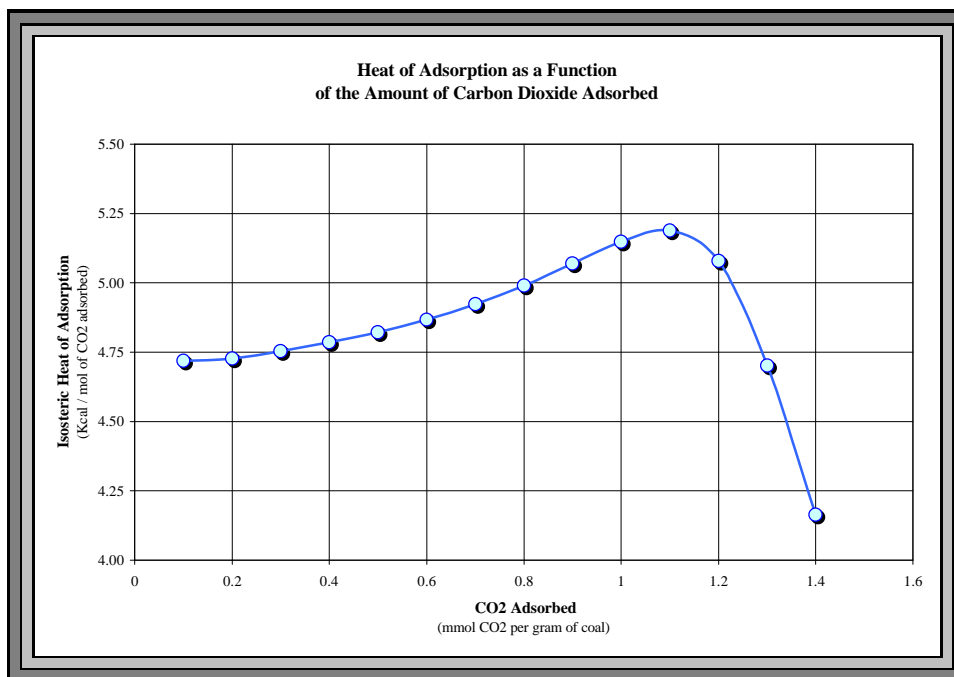




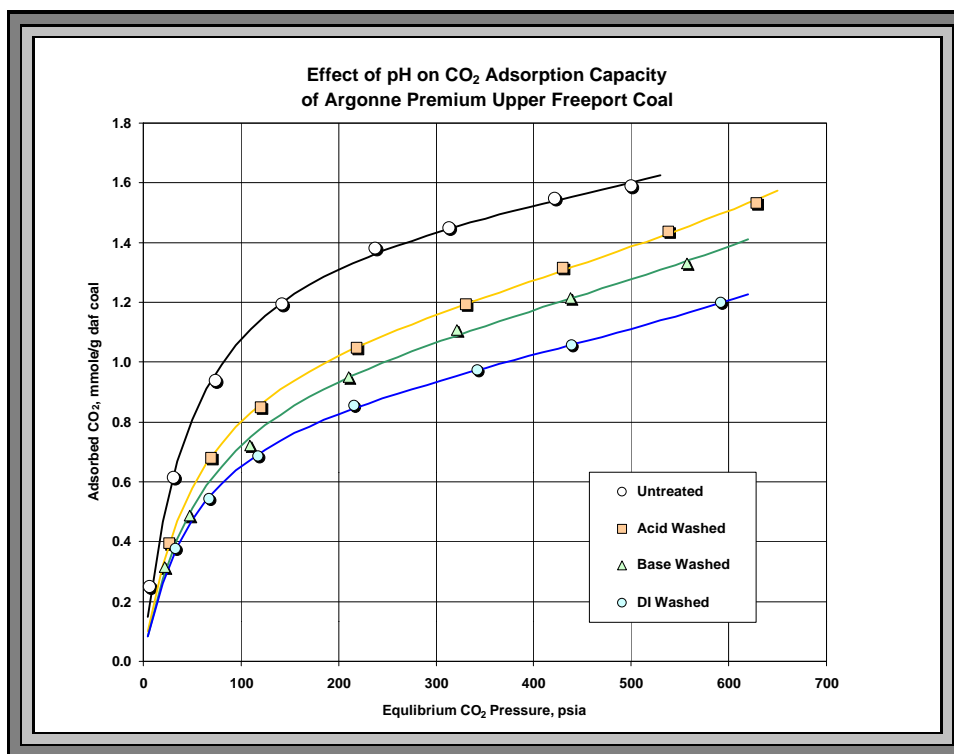
**Figure 1.** Formation of the Adsorption Isotherm by Summing the Incremental Moles Adsorbed



**Figure 2.** Effect of Increasing Temperature on the Upper Freeport Adsorption Isotherm.



**Figure 3.** Change in the Isosteric Heat of Adsorption of CO<sub>2</sub> as a Function of Coverage.



**Figure 4.** Effect of Prior Treatment on the Adsorption Isotherm of Upper Freeport Coal.