



## Moisture Sorption and Pore Collapse of Coals

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***Porosity is a common characteristic of many natural and man-made systems. The pores in these systems can have significant impact on the way materials behave and react to conditions in the environment. Coals are known to be porous in nature. This application note investigates the moisture sorption properties and pore collapse of different coal samples.***

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### Introduction

Many common materials and foods contain pores and pore networks. These can greatly impact material behavior. Nature is full of examples where pores are an integral part of living organisms and inert materials. Fruits, vegetables and plants of all types have extensive pore networks that help deliver nutrients to cells, dispose of waste and store water.

Inert materials such as soils, rocks, and minerals can exist in natural forms where porosity can play an important role in the way they behave when interacting with the environment or when subjected to processes used to convert them into useful forms for society. One such material is coal.

Coal is one of the most widely used fuels in the world. It is a widely available, cheap and reliable fuel supply, thus it accounts for 25% of the total world energy demand. In the U.S., 50% of the electricity generated comes from coal [1].

Because of its importance in providing a significant portion of the world's energy, coal has

been studied extensively over the years with many analytical techniques [1,2]. It remains a difficult material to characterize however. Coal quality is defined by its rank. There are four major coal ranks, anthracite, bituminous, sub-bituminous and lignite, in decreasing order. Because coal is generally mined from deep deposits, it can contain significant amounts of water. Removal of this water is an important step in preparation for use in power generation [2] and in processes such as coal liquefaction.

An early observation regarding water in coal was that the amount of water measured was not always reproducible and could vary depending on the method used for drying [3]. It is now broadly accepted that some coals, specifically lignites and sub-bituminous coals, have pores or capillaries that collapse upon drying and will not easily re-hydrate [4,5,6,7,8]. To demonstrate that this behavior can be observed with DVS, several coals from the Argonne Premium Coal Sample Program (APCSP) [9] were obtained and run in the DVS-Advantage instrument.



## Method

### Coal Samples

Five coal samples were ordered from APCSP: Wyodak, Beulah Zap, Illinois #6, Pocahontas #3, and Pennsylvania Upper Freeport coal. The coal types and reported water contents are listed in Table 1. The coal samples are shipped in sealed glass ampoules to preserve their original characteristics after sampling [9]. Once received at our lab, the ampoules were stored at 25° C until ready to be used. Once an ampoule was opened for sampling, the sample was taken as quickly as possible and moved to the instrument. The ampoule was quickly re-sealed and double bagged. It was then stored in a desiccator at constant humidity. Careful records of ampoule mass were kept in order to determine the extent of mass change after opening. Using this procedure, the typical mass change during subsequent samplings was +/- 0.3 wt%.

*Table 1: APCSP Coal samples with reported proximate water contents.*

Samples	Coal Type	Water Content [%]
Wyodak	Sub-Bituminous	28.1
Beulah Zap	Lignite	32.2
Illinois #6	High Volatile Bituminous	8.0
Pocahontas #3	Low Volatile Bituminous	0.7
Pennsylvania Upper Freeport	Medium Volatile Bituminous	1.1

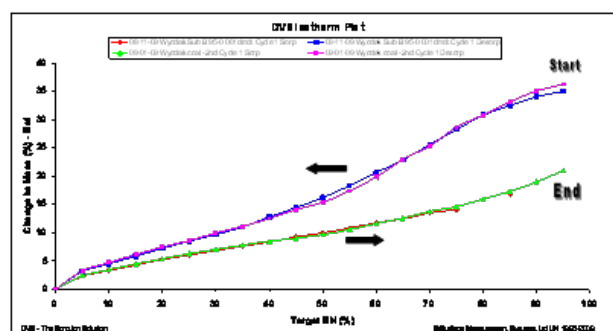
### DVS Experiments

All experiments were run on a DVS Advantage-1 instrument. Anticipating that some pores would collapse once the coal was dried; it was decided to begin the experiment at a high humidity as soon as the sample is transferred to the instrument. This is the opposite of a typical DVS experiment where humidity is stepped up from 0% RH. The humidity profile is then 95% RH → 0% RH → 95% RH in 5% RH steps. This profile should give us the maximum water content of the coal and it should also detect the collapse of pore

structure if it occurs. All experiments were run at 25 °C with sample sizes between 7 and 30mg.

## Results

Figure 1 shows the water sorption isotherms for Wyodak coal. The results are obtained in two separate experiments on different samples. The kinetic data is not shown but all steps reach equilibrium. The pink and blue lines are desorption curves, which occur first, followed by the sorption curves, green and red. The reproducibility for the two samples is excellent. The maximum water content on the desorption curves is about 35% wt. as referenced from the dry mass. The maximum water content on the sorption curves is about 20% wt. This range is in good agreement with the reported as-received water content of 28.1% and indicates that this 'as-received' coal has the capacity to uptake more moisture. But more importantly, the isotherm is consistent with the idea of pore collapse and the inability to re-hydrate the coal once it has reached 0% RH. The sorption curve does not reach the initial water content of 35% wt. as expected when pores collapse and the coal is not able to uptake as much water as it had initially.



*Figure 1. Wyodak Sub-Bituminous coal, 95-0-95% RH isotherms, two tests on fresh samples.*

The SMS Isotherm analysis macros were applied to the data in Figure 1. Using a Young & Nelson model which is part of the Isotherm Analysis package, the following fit was obtained (Figure 2). The component plot shows that a large portion of the water is absorbed and only a small portion is

monolayer or multi layer water. The quality of the fit is adequate, with a regression coefficient of 0.955,  $A=5.4 \times 10^{-4}$ ,  $B=0.013$ . The results are also listed in Table 2. This result is in good agreement with the idea that large pores and channels are part of this coal's structure (i.e. internal or bulk water).

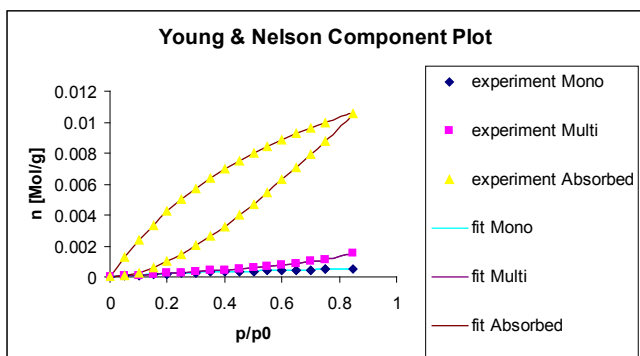


Figure 2. Young and Nelson isotherm analysis on Wyodak Sub-Bituminous coal, 95-0-95% RH at 25 °C.

The water sorption isotherms for the Beulah Zap coal sample are shown in Figure 3. Again the desorption curve in pink has the highest mass loss at 34% wt., dry referenced. The sorption curve, in light blue, has a maximum mass gain of 23.4% wt. This data is in good agreement with the reported "proximate" analysis of 32.2% wt. water for this sample, (Table 1). A second isotherm was taken on the same sample after the initial 95-0-95% RH experiment, shown below in red for sorption and dark blue for desorption. This second isotherm clearly shows that the sample will not regain its initial water once it has been lost during the first cycle. It also shows the maximum mass uptake is almost the same as the mass uptake during the sorption phase of the first cycle, light blue. Indicating that the pore collapse is essentially complete at the end of the initial desorption phase, pink.

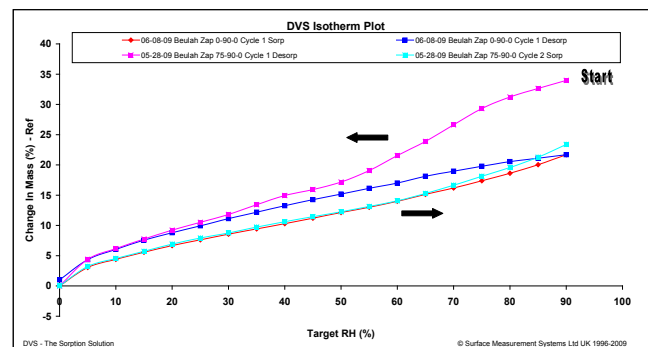


Figure 3. Beulah Zap Lignite coal, 95-0-95% RH and 0-90-0% RH isotherms.

The Young & Nelson analysis was performed on the first cycle in Figure 3. The result is similar to the previous sample (Table 2). A large portion of the water is absorbed water, while a smaller portion is multi and mono layer. This fits the view of a coal with large pore volume as expected for a lignite coal.

The higher ranked coals are thought to have predominantly small pores ( $< 10\text{\AA}$ ), these pores do not collapse when water is driven out of them and they can also be re-hydrated to a large extent [5, 6, 8, 10]. Shown in Figures 4, 5, and 6, are isotherms collected for the higher ranked coals in the same manner used above for the lower ranked coals. These coals have much lower water content than the sub-bituminous and lignite coals (Table 1). To drive all the water out of these coals it would be necessary to heat them to 105 °C for an extended period [7]. However our experiments were done at 25 °C. Even so, the isotherms show no significant change in the detected water content after the initial 95-0-95% RH experiment. The hysteresis gap is very narrow for these high rank coals, indicating water desorption is not restricted.

Pocahontas coal has a broader hysteresis in the region between 45% and 80% RH, which may indicate the presence of meso-pores.

The isotherms closely resemble Type II isotherms, in agreement with Reference 8.

The Young & Nelson result for one of these higher ranked coals, Illinois #6, is shown in Table 2. The fit shows that the major component is multi layer water, with mono layer and absorbed water making up a smaller components. This is a significantly different from the previous results on the lower ranked coals, and may be consistent with the model for coal porosity described in Reference 10. The other two high ranked coals had very similar results.

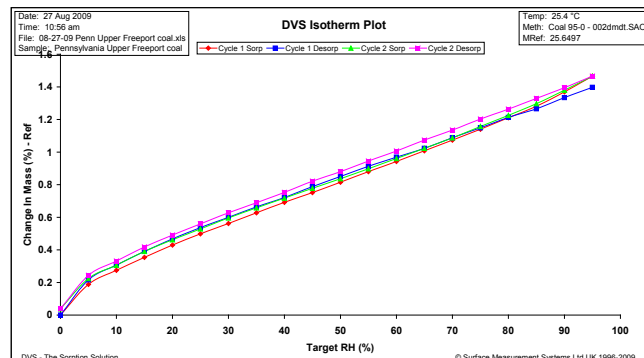


Figure 6. Pennsylvania Upper Freeport coal, 95-0-95% RH isotherms.

Table 2: APCSP Coal samples with Young and Nelson Fit Parameters.

Samples	Monolayer Water [mol/g]	Bulk Water [mol/g]
Wyodak	$5.4 \times 10^{-4}$	$1.3 \times 10^{-2}$
Beulah Zap	$2.0 \times 10^{-3}$	$1.0 \times 10^{-2}$
Illinois #6	$4.0 \times 10^{-4}$	$4.0 \times 10^{-4}$

One sample of Illinois #6 coal was run with a special experimental sequence where the first cycle was 30-90-0% RH, at 25 °C, followed by a second cycle, 0-90-0% at 25 °C, followed by in-situ heating to 110 °C for 24 hours, and finally, a third cycle was performed 0-90-0% RH at 25 °C. The isotherm results of this sequence are shown in Figure 7. The first two isotherms are nearly identical with a maximum uptake in the range of 2.3% wt. The third isotherm after heating the sample has a much wider hysteresis and is noticeably higher in uptake throughout the humidity range. Heating has driven out water from a significant portion of the small pores, making them available for mass uptake. The maximum point on the isotherm is 3.0% wt.

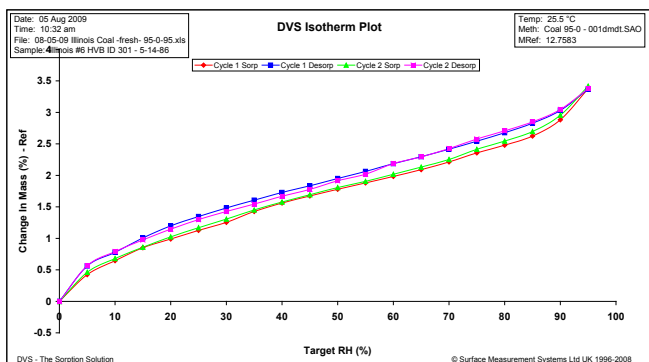


Figure 4. Illinois #6 HVB coal, 95-0-95% RH isotherms.

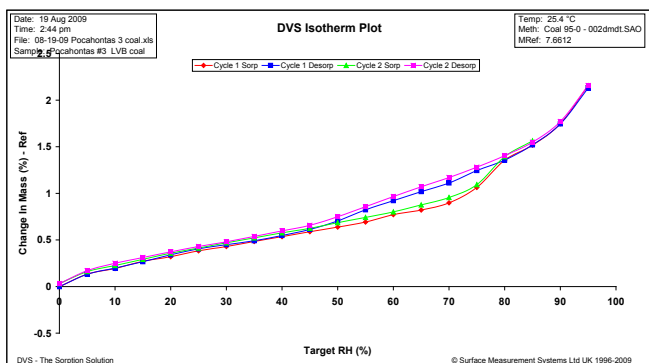


Figure 5. Pocahontas #3 LVB coal, 95-0-95% RH isotherms.

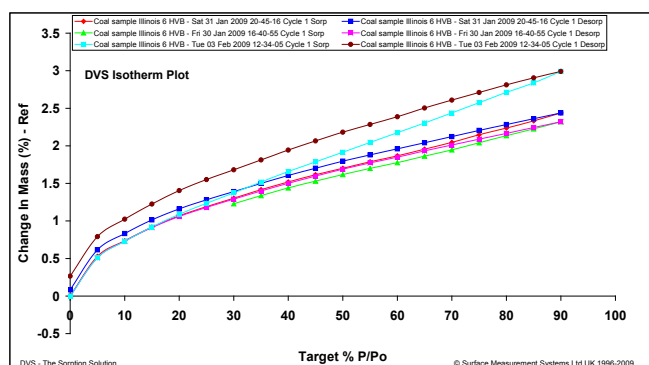


Figure 7. Illinois #6 coal, three isotherm experiment.

Some water remains in the coal after the third isotherm is completed, as evidenced by the mass not returning to its original value at 0% RH. This shows that small pores require heating to be evacuated of all water. The hysteresis curve is also noticeably wider than before, meaning water has more difficulty diffusing out from the newly opened pores. Without heating, the high rank coals behave almost like non-porous materials and have a Type II isotherm (Figures 4, 5, 6, and 7). This is because the small pores are already filled in the as-received materials. The initial hysteresis gap is small due to the pore-size distribution not being a narrow band [6]. This makes it more difficult to detect micro-porosity.

## Conclusion

A number of coals from the Argonne Premium Coal Program have been analyzed using Dynamic Vapor Sorption. By using modified experimental techniques, the presence of soft collapsible pores was detected in the low rank coals. The initial water content of these materials is easily determined using DVS. Higher ranked coals exhibit simpler isotherms. It was shown that the pores in these materials are robust and behave in a predictable manner. Isotherm modeling was applied to all the isotherms and was shown to provide useful information about the nature of the pores.

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