

KINETICS OF VACUUM DRYING AND REHYDRATION
OF ILLINOIS #6 COAL SAMPLES.
IMPLICATIONS FOR PORE STRUCTURE*

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ABSTRACT

The kinetics of vacuum dehydration and rehydration in nitrogen near room temperature have been studied with Argonne Premium Coal Samples. A block, -20 mesh and -100 mesh material were used. Three types of kinetic behavior were observed in dehydration and rehydration. These included a first order mass change, a combination of some or all of an initial linear, parabolic and final linear (LPL) segments, and a behavior which can be plotted to appear similar to an adsorption isotherm. The mechanisms involved in the linear-parabolic-linear sequence are tentatively assumed to be loss from macro pores, bulk diffusion, and loss of "bonded water" respectively. The rates are higher for dehydration in vacuum than for rehydration in nitrogen. The rates increase as the external surface increases from the block through the -20 mesh to the -100 mesh material.

INTRODUCTION

Studies of oxidation of coal at ambient conditions by measurements of weight change are complicated by the mass changes due to loss of moisture. As an initial step in determining the rate of oxidation, the kinetics of moisture loss at room temperature were measured.

Drying is also one of the oldest chemical engineering unit operations. The process involves a complex interaction of heat and mass transfer (1). If the heat transfer effects are held constant in a series of experiments, then an understanding of the mass transfer effects may be gained. In the experiments to be described the experimental arrangement was maintained in order to focus on the mass transfer involved in the dehydration and rehydration.

Moisture is believed to reside in pores in the coal structure. These pores occur with a range of diameters. The diffusion from these pores would be expected to affect the drying behavior. Gan, Nandi and Walker (2) have studied coal samples with a range of ranks and observed variation in pore sizes and volumes. The rate of diffusion in and out of these pores could provide a more complete understanding of the pore and internal structure of coal, and later lead to better understanding of the kinetics of heterogeneous reactions for coal conversion.

APPARATUS, MATERIAL AND PROCEDURE

The kinetic studies were made by placing the samples into a quartz pan, and suspending the pan inside of a quartz envelope under an Ainsworth thermobalance. The thermobalance provided electrical signals to a Bristol recorder which provided a continuous record of weight as a function of time (1" = 1 mg). The temperature was kept constant with a water bath which surrounded the sample. A weight switching mechanism provided a dynamic range of 400 mg weight change. Sample weights were in the range of 0.1 to 1 gram.

The coal samples were Illinois #6 material taken from the Argonne Premium Coal Sample Program -100 and -20 mesh material. The one-gram block was picked from a supply of material kept in chunk form, and collected at the same time and place that the Premium Sample was collected. This sample is a high volatile bituminous C rank coal with the following partial analysis:

moisture:	7.97 %
ash:	15.48 % (dry)
volatile matter:	40.05 % (dry)
carbon :	77.67 % (maf)
hydrogen:	5.00 % (maf)

In a typical run the sample was quickly weighed, transferred to the thermobalance, and the quartz envelope placed around the sample. The recorder was started, and balance released to get an initial weight reading. The vacuum pump was used to reduce the pressure to about 200 microns inside of the envelope. A buoyancy effect was observed and correction was later made for it. The weight loss was recorded, and later reduced to a table of weight and time for computer analysis using Lotus 1-2-3 or a non-linear least squares program to provide for plots, and least squares fits for these plots. After a period of time the weight loss for the sample was extremely slow, and the dehydration was halted. Rehydration was done by stopping the vacuum pump, backfilling the envelope with dry nitrogen, removing the quartz envelope, and dropping an ice cube into it. After replacing the envelope, the apparatus was evacuated, and backfilled with nitrogen to avoid contact with oxygen. The ice cube was melted, and a water bath placed around the sample for the rehydration experiment. These experiments were also allowed to continue for up to several days. For experiments involving several cycles of dehydration and rehydration, the process was started again by removing the quartz envelope, pouring out the water, drying with acetone, blowing with dry nitrogen, and replacing the envelope as quickly as possible.

RESULTS

The shape of the curve of mass loss or gain with time indicated a relatively rapid initial change which progressively became slower. Figures 1 and 2 indicate the weight change for the block on several cycles of dehydration and rehydration. The results of curve fitting efforts are also shown in the figures.

Similarly the changes and curve fitting for the -20 mesh material are indicated in Figures 3 and 4, while the results for the -100 mesh material are indicated in Figures 5 and 6.

DISCUSSION

Three types of curves were observed when the mass was plotted as a function of time. Each of these involved a rapid initial loss which gradually slowed. While the overall shape of the curves was similar, the data from these experiments fit different equations, indicating differences in the rate determining steps.

The equilibrium Langmuir adsorption isotherm has a characteristic shape. The fraction of the available surface is plotted against a concentration variable such as partial pressure. This type of curve was also seen in these kinetic studies when the fraction of the moisture adsorbed was plotted against time. The amount of moisture adsorbed is proportional to the available sites. The effect of time may be seen if the time to adsorb one half of the total moisture is used as a unit. The shape of the adsorption isotherm would indicate that if the concentration of the adsorbed gas was doubled, then the amount adsorbed would increase from $1/2$ to $2/3$. If it were tripled then the amount adsorbed would be increased to $3/4$ etc. In a similar way if the time for half sorption were doubled then the amount of sorbed gas would be increased to $2/3$. The effect of doubling the time is similar to the effect of doubling the concentration. The label "adsorption" has been applied in the data analysis of data which fit this type of curve.

For a unimolecular reaction of a gaseous reactant on the surface of a solid, the rate is proportional to the fraction of the surface covered by the gas. At the beginning of the adsorption the water molecules are adsorbed on the bare surface and the rate is a maximum, governed by the vapor pressure of the water and the external surface accessible to the gas. However the equation applies over a time long enough to adsorb or desorb most of the water which implies a rapid transfer of moisture from the external surface to the interior. The rate is reduced and can be characterized by a time to reach a reduction by one half. The label "first order" has been applied to data which fit this type of curve.

The analysis of the data also indicated a behavior in which the mass change was resolved into three distinct regimes of weight loss. The initial one involved a linear weight loss with time. The second regime involved a parabolic weight loss with time, and the third regime was another linear loss with time, but with a much smaller slope than the first linear one. This was seen in the second dehydration of the -20 mesh material. The label "linear-parabolic-linear" or "LPL" has been applied to data which fit this type of curve. In some cases, such as rehydration of the block, the initial and final linear segments were very short or absent.

The 1.0 gram block was obtained from a 5-gallon storage container kept under nitrogen. The conditions of collection and storage permitted some drying of the sample during the oxygen removal,

and transfer between containers. The initial dehydration was followed by a dehydration, and the cycle was repeated. The sample was then left under nitrogen in contact with saturated water vapor for three weeks. The subsequent (third) dehydration indicated that the sample had acquired a substantially larger amount of water than it possessed during either of the earlier experiments. A second cycle followed the dehydration. The arrows on Figure 1 indicate the relationship between the pairs of dehydration cycles.

The data analysis for the four cycles gave these results:

Cycle	Dehydration	Rehydration
First:	Adsorption	Parabolic
Second:	Adsorption	Parabolic
Third:	Adsorption	Parabolic
Fourth:	Adsorption	Not Done

The data analysis for the dehydration indicated that the fit was better for the adsorption type curve than either of the first order or a combination of the LPL curves. The initial portion of the adsorption curve frequently is linear on the chart paper, and is believed to involve transfer of moisture from the external surface or pores. The weight change required for a monolayer of moisture as typically determined by nitrogen adsorption is about one half milligram per gram of coal. The actual loss is larger than this by an order of magnitude, indicating that the surface moisture is replenished by large open pores. The further loss of moisture is assumed to involve a "bulk diffusion" mechanism. For a solid with a consistent set of pores or defects for diffusion a parabola is observed in a plot of weight change with time. The lack of a fit to a parabolic curve and more rapid decrease in rate than predicted from a parabolic fit is believed to be due to either to diffusion from progressively smaller pores with smaller diffusion constants or to blockage of pores. The data also indicate that the rate is dependent upon the amount of water which is available in the particle. This was especially noticeable after the extended rehydration between the second and third dehydration. The pores were not irreversibly collapsed but were able to accumulate a larger moisture content than was present at the beginning of the experiment. This amount exceeded the ASTM moisture determination.

The analysis for rehydration indicated a better fit for the parabolic equation. The rate for rehydration is significantly less than for dehydration. The minimal amount of linear contribution to the initial mass change indicates that the external surface was quickly covered and subsequent reaction was limited by diffusion through a growing interface layer. This layer may have been a set of blocked pores. The external surface is a minimum for a sample which is a single particle.

The -20 mesh sample was 0.100 grams of a supply kept in a plastic bottle filled from incompletely sealed ampoules. The material had been exposed to the drier atmosphere in the laboratory. The initial dehydration did not remove much moisture since much of it had already been lost. The rehydration restored a considerable amount of the moisture content, and led to a higher rate and a modified curve shape (LPL) for the second and third dehydrations.

The rehydration rates showed a very similar set of curve shapes, and a gradually diminishing rate due to progressive internal changes. Although the curve shapes for the rehydration were similar, the agreement with the adsorption type curve was clearly better than first order for the first two curves, and somewhat better for first order for the third curve.

The data analysis gave the following results:

Cycle	Dehydration	Rehydration
First:	First order	Adsorption
Second:	Linear-Parabolic-Linear	Adsorption
Third:	Linear-Parabolic-Linear	First order

The three regimes in the second and third dehydration indicate that three mechanisms of water loss were occurring during the dehydration. The initial linear loss is believed to be due to the loss of surface water from the external surfaces and macro pores. The parabolic weight loss is believed to be due to bulk diffusion from the coal of "dissolved" water. This water is believed to be caught in very small cavities or imperfections in the packing structure of the coal. These cavities can provide a temporary site for molecules as they diffuse from the bulk to some surface accessible to the external pores. The dynamic motion of the coal "molecules" may permit the opportunity for the water molecules to migrate from one site to another on the way to the external surface. The third regime, involving the second linear portion is believed to be due to the release of water from sites involving "bonded water". The low temperature provides relatively little thermal energy to permit release of the water, but enough to permit a measurement.

Assuming that the pores are filled with water, one can obtain a measure of the macro pore volume by calculating the moisture loss per gram of coal, and using the density of water. Similarly, one can obtain a measure of the "dissolved" water" by noting the weight of the water lost during the parabolic part of the total weight loss curve, and calculating the loss per gram of coal. Again, in a similar way, one could make the calculation for the "bonded water". This portion would represent the water tied to functional groups, or hydrogen bonded.

The first type of water should be "freezable" while the latter two should not have the properties to permit observation of freezing behavior. Freezing is a bulk property, and would require a number of molecules to demonstrate the existence of a solid crystalline material. Individual molecules, separated from other similar molecules would not be able to demonstrate this behavior.

The -100 mesh material was a 0.239 gram sample which had been equilibrated with water for at least 5 days at room temperature. The two dehydration runs fit the adsorption type curve. The two rehydration runs initially followed this type of curve, but later exhibited a more rapid rate and departure from the curve. This behavior is indicative of multilayer formation in the type IV adsorption isotherm, and may indicate a similar phenomenon here. The rates for the second dehydration or rehydration are lower than those for the first run in the cycles. The incremental

change in weight with time toward the end of the run is greater for the second run indicating a tendency to continue and possibly achieve a similar weight gain or loss over a very extended time. For these samples the initial dehydration proceeded with a higher rate than the second. The sample did not take up as much water during the rehydration as it lost during the initial dehydration.

The data analysis gave the following results:

Cycle	Dehydration	Rehydration
First:	Adsorption	Adsorption + multilayer?
Second:	Adsorption	Adsorption + multilayer?

CONCLUSIONS

The rates of dehydration and rehydration near room temperature are complex. The specific form of the equation describing the rates varies depending on the particle size and history of the sample. Several rate equations can be used to provide a "best fit" to all of the data. Blocks of vacuum dried coal will continue to absorb significant amounts of water over a period of weeks at room temperature. The pores in the block were not irreversibly collapsed in a manner that prevented restoration of the moisture content.

The rate of dehydration in vacuum for a given sample is faster than the rate of rehydration in nitrogen. The presence of nitrogen apparently interferes with the rehydration.

The vacuum dehydration of the block of coal followed a first order curve. This is consistent with loss of moisture from the equivalent of a surface with all of the moisture initially upon it. The rehydration of the block follows a parabolic curve, which is consistent with a diffusion controlled process. This would be observed if the moisture diffused into the block through a layer which consisted of swollen pores, and the pores continued to swell as the moisture continued to diffuse. The behavior of the block is believed to represent the behavior of an independent particle. The -20 mesh vacuum dehydration followed a first order curve for most of the vacuum dehydration and one rehydration in nitrogen. The initial two rehydrations followed the adsorption type curve. This behavior is consistent with the limitation on moisture loss due to a transfer from a surface with all of the moisture initially on it, or surface sites equally accessible during rehydration. The appearance of the LPL sequence indicates that the rehydration put enough moisture back into the sample to allow some differentiation of the several mechanisms that were operative. Rehydration initially indicates adsorption to saturate the surface, and may be augmented by particle-particle interaction. The behavior of this sample is believed to reflect the behavior of a sample consisting of many small particles, and which has been exposed to some drying and atmospheric oxidation. The -100 mesh samples had been equilibrated with moisture, and showed an adsorption type of curve on both dehydration and rehydration. The initial steep part of the curve is attributed to the saturation of the surface with moisture. The moisture may be going to junctions between particles. The rehydration curves show evidence for multilayer adsorption as part of their shape.

The behavior of this sample is believed to reflect the behavior of a sample which consists of small particles, has been protected from oxidation and has been given an opportunity to adsorb moisture to achieve near equilibrium at the experimental temperature.

The use of several equations to give a fit to the data prevents a direct comparison of rates. However, one can rank the rates for the different particle sizes by establishing the time required to lose or gain half of the moisture over a reasonably long period of the experiments to be compared. If it is assumed that the -20 or -100 mesh particles would behave in the same manner whether 0.1 or 1 gram were used, then the rates are dependent on particle size, and increase from the block through -20 mesh to -100 mesh. This behavior indicates that the external surface area is important in the overall rates for both dehydration and rehydration.

FUTURE WORK

It is intended to extend this work to the full set of the Argonne Premium Coals over a range of temperature to establish the similarity in behavior, effects of rank, and observe any special behavior that may be found for the low rank coals due to gel structure that may be present in them. In addition it is intended to observe the weight changes following vacuum drying upon introduction of other gases including those which are normally used to establish the surface area.

ACKNOWLEDGMENTS

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REFERENCES

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2. Gan, H., Nandi, S. P., and Walker, Jr., P. L., Fuel, 51, 272(1972).

FIGURE CAPTIONS

These are as indicated. Weight change in milligrams is plotted on the vertical axis, and time in minutes on the horizontal axis. Symbols indicate observed points. Lines indicate calculated values for the curves indicated in the text. The numbers adjacent to the curves indicate the cycle.

Figure 1. Vacuum Dehydration of IL #8 Coal Block
22 C. - 11.0012.83

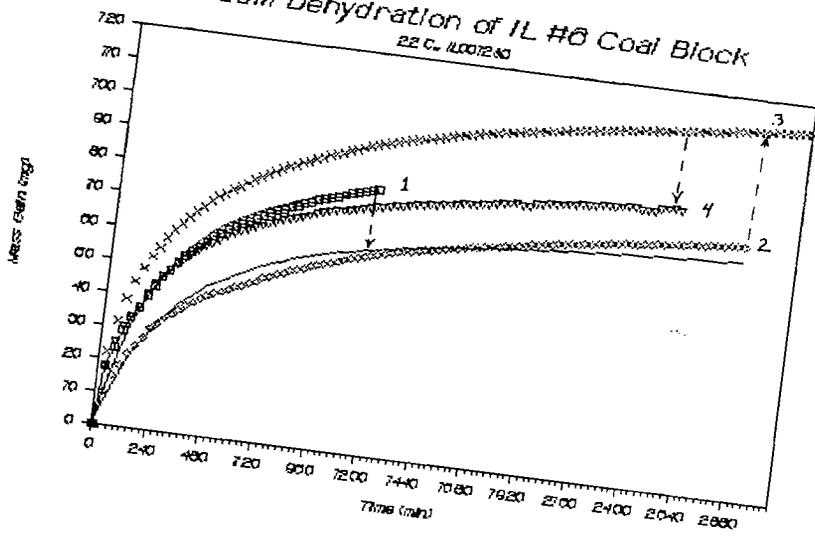


Figure 2. Rehydration of IL #8 Coal Chunk
22 C. - 11.0012.83

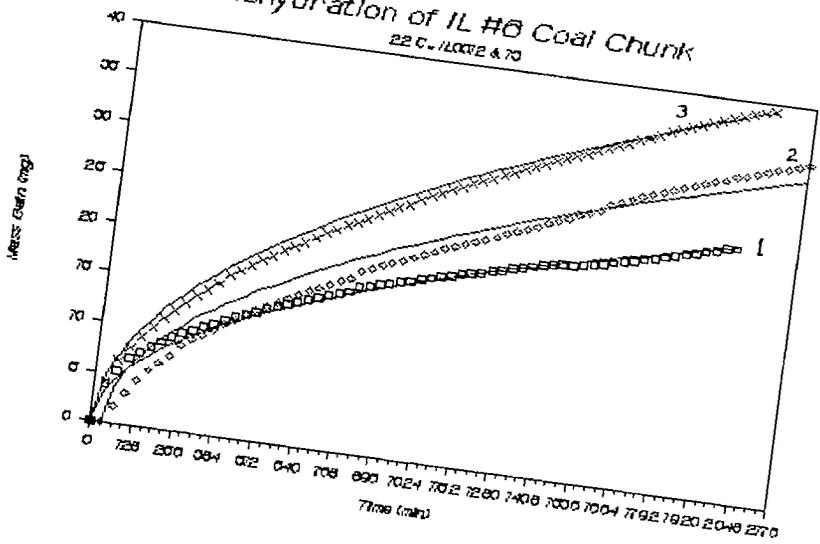


Figure 3. *Vac. Dehydration IL#6, -20 Mesh*
Obs. 1st Order & Lin-Parab. IL2000

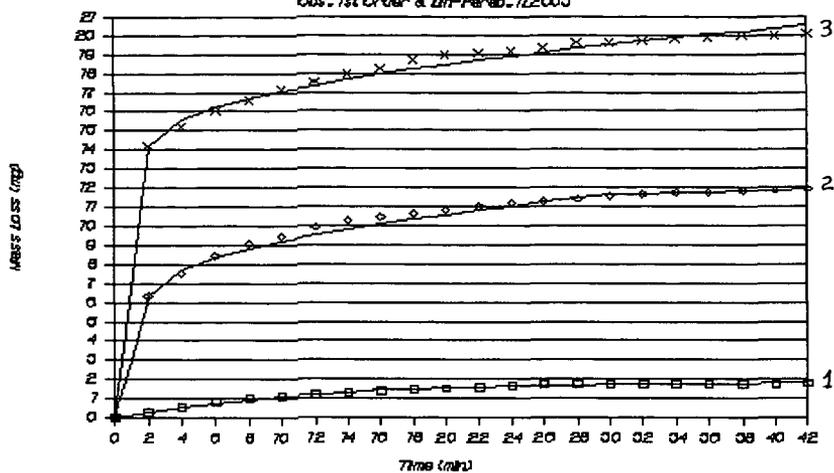


Figure 4. *Rehydration of IL#6 In N₂, -20 Mesh*
Obsd & Ads. 1st Order, IL2000, /20 mesh/

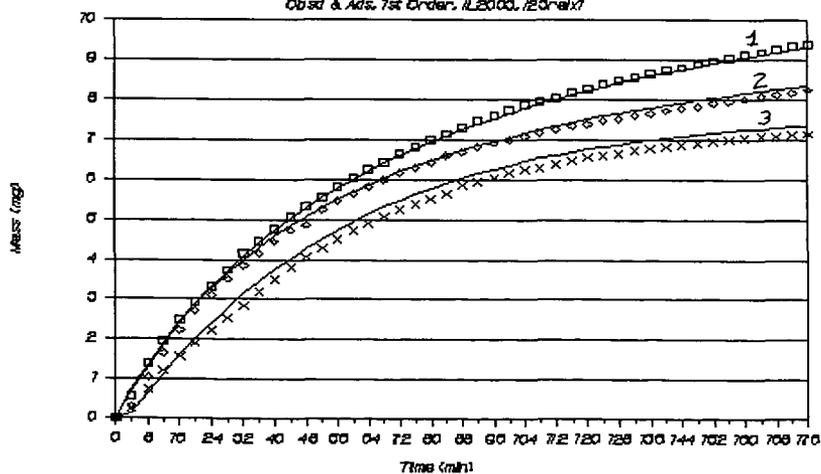


Figure 5. Vac Dehydration of IL #6 -100 Mesh

22 C. 11/07/02

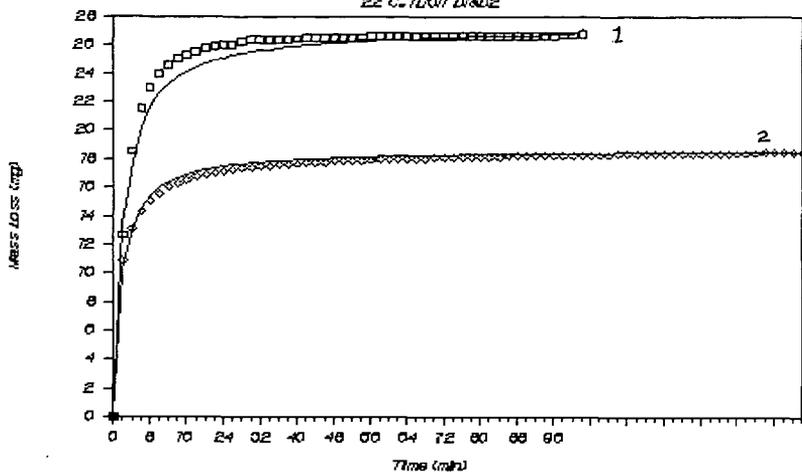


Figure 6. Rehydration of IL #6 -100 Mesh In N2

23 C. 11/07/02

