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DRYING OF BEULAH ZAP LIGNITE

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INTRODUCTION

The drying of low rank coal is important in effective liquefaction of this abundant resource. It has been said by several researchers that a small reduction of moisture in these coals does not adversely affect the liquefaction behavior, however a very large amount of drying does have an adverse effect on the rates of this reaction. It has been felt that this behavior may be due to the possible irreversible change in physical pore structure that was believed to accompany drying.

It is generally recognized that the physical structure of coal is composed of three components: an organic matrix, inorganic matter, and an extensive network of pores. It is also believed that the pore network usually contains water in 'as-mined' coals. Mraw and Silbernagel (1) suggested that the amount of water present in as-mined coals provides a measure of pore volume. However, Kaji et al. (2) examined the water-holding capacity, specific surface area, and pore volume of 13 coals from various locations, ranging from lignite to anthracite, and found no correlation between the water-holding capacity and the pore volume. Based on the assumption that the total coal oxygen is distributed uniformly through the coal and the functional-group oxygen increases with oxygen content, Kaji et al. found a linear relationship between the hydrophilic sites and the water-holding capacity of coal. It seems to us that the relationship between the total oxygen content of coal and the water-holding capacity is more fortuitous than real since oxygen-functional groups are not the only hydrophilic sites in coal (3). Moreover, the presence of minerals, especially smectite lattices, and various cations will also strongly influence the coal-water interactions.

Vorres et al. (4) and Vorres and Kolman (5) adopted the approach of ascertaining the kinetics of vacuum drying of coal as a means to understand the complex coal-water interactions. From isothermal thermogravimetry analysis, i.e., the weight loss vs. time at fixed temperature, Vorres and his co-workers indicated that the dehydration of Illinois No. 6 in the form of a block, -20 mesh, and -100 mesh, follows a desorption kinetics mechanism. Thus, they concluded that the rate controlling mechanism of dehydration is governed by the surface of coal. In addition, Vorres and his co-workers indicated that the particle size and the history of coal also affect the dehydration kinetics of coal. More recently, Abhari and Isaacs (6) used the thermogravimetric

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analysis (TGA) technique to explore the drying kinetics of six coals from the Argonne coal-sample bank. They evoked a bulk moisture/pore moisture model to explain the observed drying kinetics for the six coals, in which the order of kinetics, i.e., the order of dehydration showed a strong dependence on the rank of coal. In calculating the kinetics parameters from the weight loss data, these researchers assumed that water in coal is held by the physisorption process. This assumption is at variance with the temperature dependent NMR results (7) and the contention of Kaji et al. (2).

In this paper, we report our recent results on the kinetics of water's desorption from Beulah-Zap lignite coal, as determined by thermogravimetric analysis (TGA) and the differential scanning calorimetry (DSC) technique. The kinetic analysis of DSC was further complimented by determining the mechanism of air drying of lignite coal with the help of an in-situ Desorption Kinetics via Fourier transform infrared (ISDK-FTIR) technique.

EXPERIMENTAL

Isothermal Thermogravimetry

Coal drying was done with a Cahn model 121 thermobalance attached to an IBM PC/XT microcomputer. Vendor-supplied software was used to monitor the progress of individual runs, and convert data files to a form that could be further studied with Lotus 123.

The data were obtained as files of weight at 10 second intervals. For runs longer than 10 hours, the runs were modified to work with data points at 20 second intervals.

The typical sample size was about 140 mg. The sample was placed in a platinum hemispherically-shaped pan. Sample sizes included the two mesh sizes of the usual Argonne Premium Coal Samples (-100 and -20 < 841u) and also one or two small pieces which came from lumps which have been stored under nitrogen since the time of the acquisition of the original samples. A sample of -400 mesh (< 37u) material was prepared at Southern Illinois University at Carbondale with a Brinkmann Micro-Rapid mill.

Data were analyzed by testing the weight loss as a function of time with 13 different kinetic expressions including geometrical, unimolecular, first and second order diffusion to establish a best fit. Lotus 123 was used for analysis of individual run data.

Samples were quickly transferred from freshly opened ampoules or bottles which had been kept in constant humidity chambers with water at room temperature (293°K). In the thermobalance system a period of 5 minutes was used to stabilize the system and initiate data acquisition. Room temperature runs were made with and without the furnace in place. The furnace was used for runs at 313 and 353°K.

For comparison, a run was made at room temperature under vacuum with the -20 mesh material.

The gas atmosphere was cylinder nitrogen (99.99%) used without further purification and passed over the sample at a rate of about 100 cc/min.

Differential Scanning Calorimetry (DSC) Measurements

The kinetics of water's desorption from lignite coal was evaluated using a non-isothermal approach in which the coal sample temperature was progressively raised at a constant heating rate (8-10). Janikowski and Stenberg (11) and Elder and Harris (12) from their DSC measurements have shown that when coal samples are subjected to thermal treatment a broad endothermic peak is observed at around 323 K - 423 K. This broad peak has been associated with the water loss from the coal. Therefore, a careful DSC experiment at $300\text{ K} < T < 473\text{ K}$ under inert environment can provide information on the kinetics of water's desorption from coal. We chose -20 mesh and -400 mesh particle size coal to explore the kinetics of water's desorption from coal. The as-received sample of Beulah-Zap lignite coal was of -20 mesh size, and the sample was received in a sealed ampule. A part of the -20 mesh coal sample was ground in a Brinkmann Micro-Rapid mill to reduce its particle size to -400 mesh. The ground sample was sieved through a -400 mesh sieve, and the -400 mesh particles were collected for DSC measurements.

The desorption of water from -20 mesh and -400 mesh particle size lignite coal was determined with the help of a well calibrated (13,14) Perkin-Elmer DSC7 system. Prior to recording the DSC curves, the lignite coal samples were kept at a 93% relative humidity (RH) for 48 hours in a humidity controlled chamber. Afterwards, about 20 mg of the samples were accurately weighed on a microbalance. The samples were then loaded in Al pans and sealed with the help of Al lids. A number of holes were drilled in the Al lids to ensure the easy escape of water vapors from the Al pans. In loading the coal samples in the Al pans, extreme care was exercised so that mechanical compacting of the particles did not control the overall desorption kinetics of water. The DSC curves were recorded at a heating rate of 10 K/min. under the controlled He purge. After the DSC runs, the sample pans were again weighed to ascertain weight loss due to the thermal treatment.

In-situ Desorption Kinetics via Transmission-FTIR (ISDK-FTIR) Measurements

The air drying kinetics of Beulah-Zap lignite coal was determined using the ISDK-FTIR technique (15). In this approach, a thin film of coal (particle size -400 mesh) was painted onto a laser grade ZnSe optical flat. The thin film was equilibrated at 93% RH in a humidity controlled chamber for 48 hours at room temperature. The desorption kinetics of water from coal was determined by mounting the coal sample in the FTIR spectrometer's sample chamber. The sample chamber was purged with a controlled flow of dry air in order to maintain a constant humidity of 9% RH. The FTIR spectra of coal were recorded as a function of time in the transmission mode. The spectra were collected by employing a fast scanning (25 scans/sec) Nicolet 740 FTIR spectrometer with a fast response liquid nitrogen cooled MCT detector. One hundred interferograms were collected at 4 cm^{-1} resolution to produce the

coal sample's FTIR spectrum. To monitor the desorption kinetics of water, a Nicolet 620 computer, interfaced with the spectrometer, was programmed to collect 100 interferograms after an interval of every 48 seconds. After the collection of 20 spectra, the time interval was increased to 80 seconds for the next 20 spectra and then subsequently to a time interval of 180 seconds. The collected interferograms were stored on a hard disk and after the completion of the experiment, the interferograms were Fourier transformed and co-added to produce the desired FTIR spectrum.

RESULTS AND DISCUSSION

Isothermal Thermogravimetry

The data were normalized to one gram of starting sample weight. The best fit of the data were obtained with a unimolecular decay kinetic expression. Plots of \ln (water left) versus time gave a characteristic shape. The plot indicates a consistent slope for about 85% of the moisture loss of the coal. A transition then occurs. The rate is then reduced to about half of the earlier rate. The kinetic parameters are given in Table 1. Values of R squared in the regression coefficient from Lotus 123 were greater than .99 for all but two of the runs. Rate coefficients, k , were obtained from the rate of change of the \ln (water left) in mg water/gram of original sample as a function of time in seconds. For a number of runs, the data did not initially fit the straight line. For these, the data included in the determination of the rate constant did not start at zero. The range of time included for the determination is indicated in the table. In the cases of initial lack of fit the rates were always above the line, indicating a more rapid moisture loss.

In general the highest R squared values are associated with the data obtained from the blocks, indicating a greater consistency with data from a singular piece of material.

The use of vacuum to remove moisture is seen to be capable of much more rapid removal of water than a stream of dry nitrogen. The ratio of the rate coefficients is an order of magnitude greater, and would imply an rate advantage to this technique for engineering for rapid processing of pulverized fuel.

The initial removal of about 85% of the moisture and then a transition to a slower rate of water loss implies a structural rearrangement. It is believed that the pores of the particles are changed after this amount of water is lost in a manner that makes the further loss of water more difficult.

DSC Results

Figure 1 reproduces the DSC curves obtained at a heating rate of 10 Kmin^{-1} for -20 mesh and -400 mesh particle size Beulah-Zap lignite coal. As pointed out earlier, Janikowski and Stenberg (11) observed similar endothermic broad peaks in their DSC curves at $323 \text{ K} < T < 423 \text{ K}$ from various lignite and subbituminous coal samples. At $323 \text{ K} < T < 473 \text{ K}$, water is expected to be desorbed

from the coal sample. It is worthwhile to point out here that vacuum dried samples of Beulah-Zap lignite coal showed no exothermic peaks at $323 \text{ K} < T < 473 \text{ K}$. Therefore, consistent with the observations of Janikowski and Stenberg, we also believe that the broad peak at around 373 K , as seen in Fig. 1, is produced due to the water loss from coal.

The general kinetic expression for the decomposition of a solid is

$$\frac{d\alpha}{dt} = A \exp(-E/RT) f(\alpha). \quad (1)$$

In Eq. 1, α is the fractional conversion at a time t , k is the rate of reaction, E is the activation energy in J/mol, R is the gas constant in J/mol.K, A is the frequency factor, and T is the temperature in K. Since our DSC measurements were conducted in a non-isothermal mode, Eq. 1 was modified to take into account the constant heating rates used, i.e.,

$$\frac{d\alpha dT}{dT dt} = A \exp(-E/RT) f(\alpha). \quad (2)$$

Substituting B for the constant heating rate dT/dt used, Eq. 2 can be rewritten as

$$\frac{d\alpha}{dT} = \frac{A}{B} \exp(-E/RT) f(\alpha). \quad (3)$$

Rearranging and integrating Eq. 3, we obtain

$$F(\alpha) = \frac{ART^2}{BE} \left(1 - \frac{2RT}{E}\right) \exp(-E/RT). \quad (4)$$

and

$$F(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}. \quad (5)$$

Eq. 4 can be further simplified by taking logs, i.e.,

$$\ln\left(\frac{F(\alpha)}{T^2}\right) = \ln\frac{AR}{BE} \left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \quad (6)$$

The fraction of the sample reacted, i.e., α , was determined by measuring the ratio of the partial area at temperature T to the total peak area of the appropriate DSC curves shown in Fig. 1. The isothermal kinetic expressions, given in Refs. 16 and 17, representing various decomposition models were converted into non-isothermal kinetic expressions to determine the desired $F(\alpha)$ functions. The experimental data was then fitted to 12 non-isothermal kinetic models depicting geometrical models, the Unimolecular model, sigmoid rate models, diffusion models, and the 2nd order-diffusion model. A least squares procedure, in conjunction with Eqs. 4, 5, and 6, was adopted to ascertain the kinetics mechanism of water's desorption from lignite coal. Our calculations suggest that the Unimolecular kinetic model and 2nd-order diffusion kinetic model are simultaneously operative for the desorption of water from -20 mesh Beulah-Zap lignite coal; while for -400 mesh particle size coal, only the 2nd-order diffusion mechanism is effective. The activation energy barriers for Unimolecular decay and 2nd-order diffusion models were determined from Eq. 6. For -20 mesh particle size lignite coal the activation energies associated with Unimolecular decay model and 2nd-order diffusion model were 54 KJ/mol (12.94 Kcal/mol) and 78.5

KJ/mol (18.8 Kcal/mol), respectively. The activation energy of the 2nd-order diffusion model for - 400 mesh particle size Beulah-Zap lignite coal was 88.2 KJ/mol (21.1 Kcal/mol). The individual contributions of these kinetic models to the overall desorption of water from lignite coal were determined by fitting the experimental data to the temperature dependence of $\alpha(T)$, i.e.,

$$\alpha(T) = C_1(1 - \exp(-Y(T))) + C_2\left(1 - \frac{1}{Y(T)+1}\right), \quad (7)$$

where, $C_1 + C_2 = 1$, and

$$Y(T) = \frac{ART^2}{BE} \left(1 - \frac{2RT}{E}\right) \exp(-E/RT).$$

In Eq. 7, the first term on the right hand side represents the Unimolecular decay kinetics, while the second term depicts the 2nd-order diffusion kinetics. C_1 and C_2 for -20 mesh particle size coal were 0.23 and 0.77, respectively, while for -400 mesh particle size $C_1 = 0$ and $C_2 = 1$. Figure 2 compares the experimentally observed $\alpha(T)$ with the calculated values for -20 mesh and -400 mesh particle size Beulah-Zap lignite coal. As can be seen from Fig. 2, the agreement between the calculated values and the experimentally observed values is excellent.

The Unimolecular decay kinetics of decomposition of a solid represents a system in which each molecule has an equal probability of undergoing decomposition. In a complex system like lignite coal, the bulk type water, present as a film around the particle or present as pore water in large pores, is expected to display evaporation like characteristics. This should be especially true for water which is away from the surface of coal or is around or near the mouth of large pores. Consequently, it is argued that the observed Unimolecular decay kinetics for -20 mesh particle size coal represents the loss of bulk type water from the Beulah-Zap lignite coal. The 2nd-order diffusion kinetics represents a recombination process in which product molecules are produced with excess energy. The excess energy is then utilized in re-energizing the reactant molecules. It seems to us the water molecules hydrogen bonded to the oxygen functional groups in narrow pores and surface water in large pores will desorb via the 2nd-order diffusion mechanism. As the particle size of coal is reduced to - 400 mesh from -20 mesh, the large pores concentration in coal sample is expected to decrease. Therefore, the observation of desorption of water from - 400 mesh particle size coal via 2nd-order diffusion mechanism is not unreasonable.

ISDK-FTIR Results

Figures 3 and 4 show the observed desorption kinetics of water at $T = 294$ K from the - 400 mesh particle size Beulah-Zap lignite coal in the water's stretching and bending regions, respectively. The desorption results can be summarized as follows: (1) Three broad vibrations were observed in the O-H stretching region at 3614, 3373, and 3222 cm^{-1} as reflected by the FTIR difference spectrum at t min., i.e., FTIR spectrum at 0 min. - FTIR spectrum at t min. In the water's bending region, positive bands at 1628, 1552, 1458, and 1384 cm^{-1} and a negative band at 1740 cm^{-1} were

found in the difference spectrum. The observed desorption kinetics for the water's stretching and bending modes are shown in Fig. 5. Attempts were made to determine the desorption kinetic mechanism(s) for 3614, 3373, 3222, and 1628 cm^{-1} bands by subjecting the intensity loss data to 12 desorption kinetics models as described in Refs. 15, 16, and 17. All the water bands, be they stretch modes or bend modes, displayed a 2nd-order diffusion mechanism. Therefore, our ISDK-FTIR results support and are consistent with our conclusion from DSC measurements that water from small particles of lignite coal desorbs via a 2nd-order diffusion mechanism.

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Table 1.

Kinetic Coefficients for Beulah-Zap Lignite

(k values are in units of 10^{-5} mg water/gm original sample sec^{-1})

Data at 293°K

Run#	Mesh	k	duration (sec)	R squared
2	-100	9.0	9,000-20,000	.99993
4	-100	10.	0-19,000	.9996
14	-20	10.	0-20,000	.9998
18	Block	11.	0-	.998
22	-20	7.0	2,000-8,000	.97 +
23	-100	7.0	5,000-23,000	.9998
24	Block	10.	0-6,000	.99997
25	-400	11.	5,000-8,000	.9992
26	-400	11.	0-8,000	.9993
27	Block	8.0	0-12,000	.999991

Data at 313°K

Run#	Mesh	k	duration (sec)	R squared
3	-100	24.	1,000-7,000	.998
6	-100	14.	2,000-8,000	.97 +
11	-20	24.	3,000-9,000	.998
16	Block	23.	2,500-5,500	.9990
19	Block	19.	1,000-9,000	.9995

Data at 353°K

Run#	Mesh	k	duration (sec)	R squared
5	-100	99.	700-2,700	.997
7	-100	127	700-2,100	.9990
10	-20	131	900-2,100	.997
15	Block	85	1,100-2,900	.9994

Run in vacuum at 293°K

Run#	Mesh	k	duration (sec)	R squared
V6	-20	108.	1,000-3,000	.997

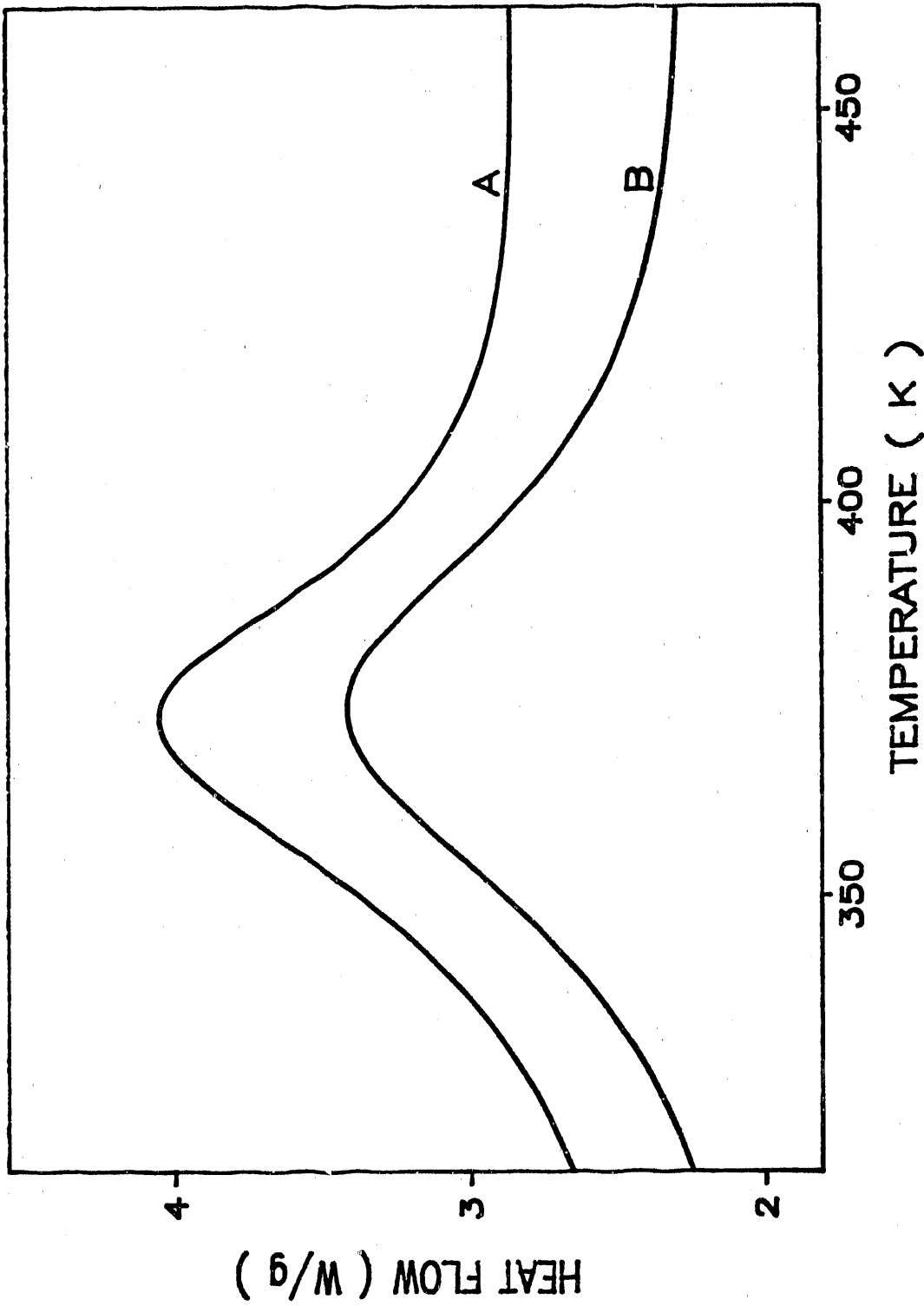


Fig. 1 The DSC curve shows the endothermic peak due to the desorption of water from Beulah-Zap lignite coal. (A) < 841 particle size, (B) < 37 particle size.

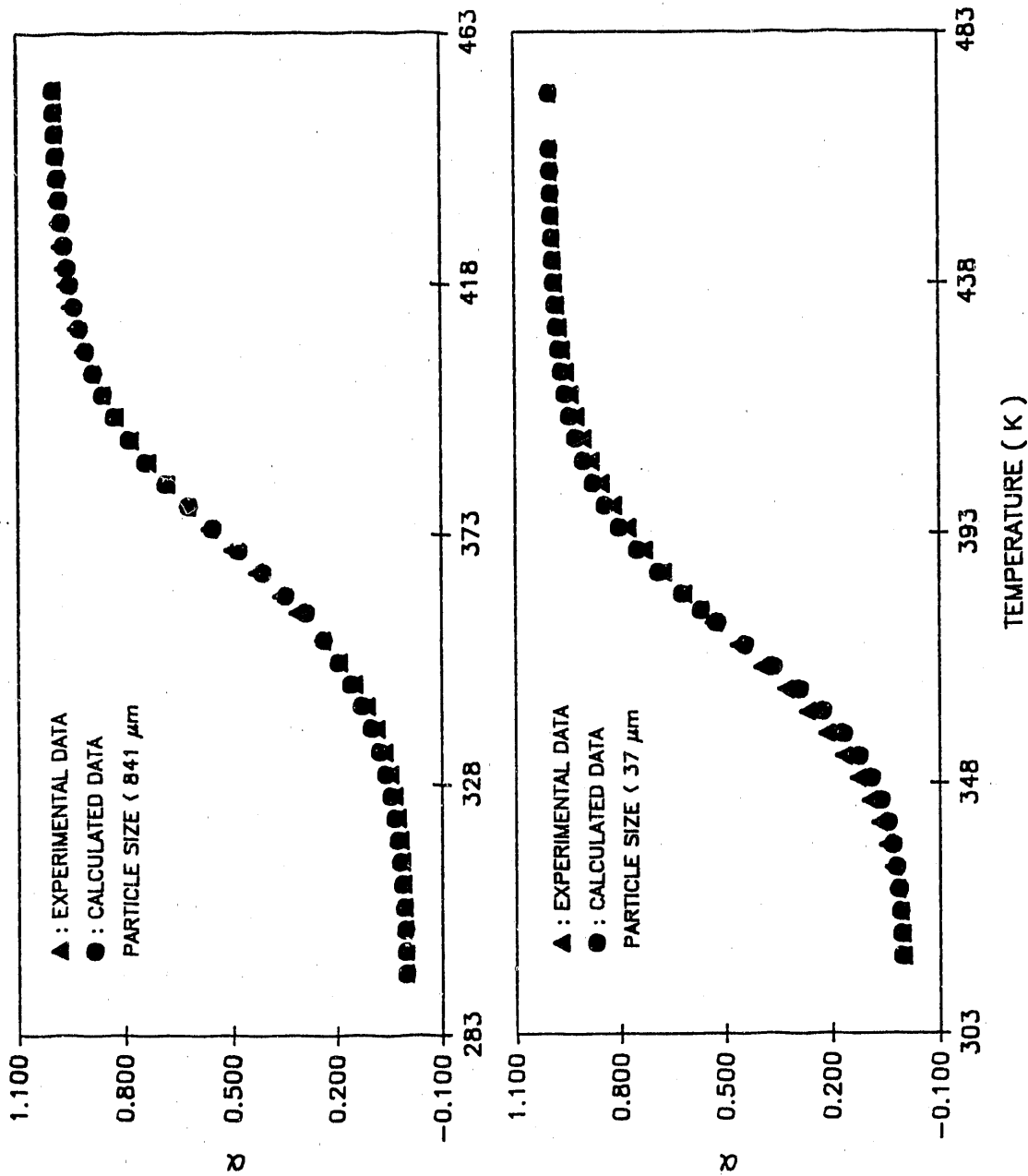


Fig. 2 This graph compares the experimentally observed desorption of water data with calculated values of Eq. 7.

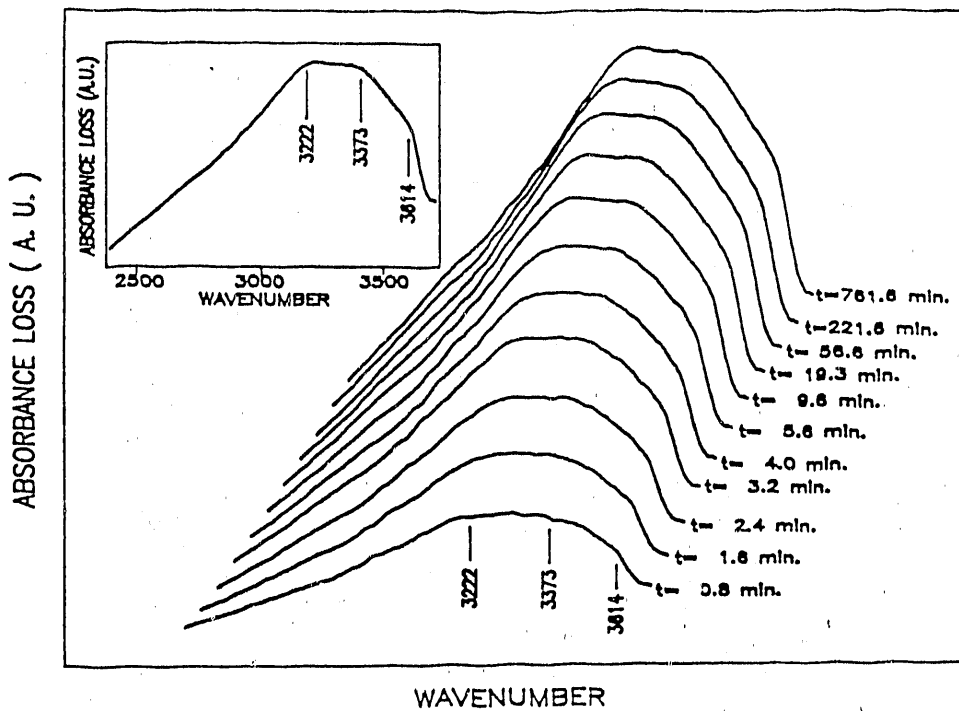


Fig. 3 FTIR difference spectra at t min. show the desorption kinetics of various types of water from < 37 particle size Beulah-Zap lignite coal in the water's stretching region.

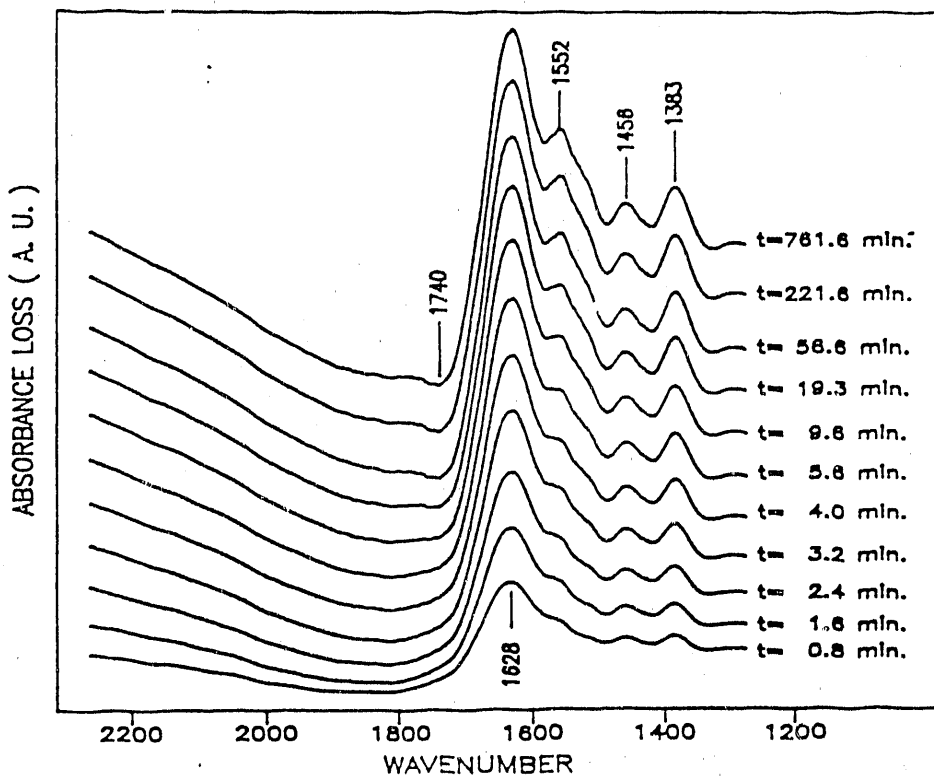


Fig. 4 FTIR difference spectra at t min. show the desorption kinetics of water from the lignite coal in the water's bending region.

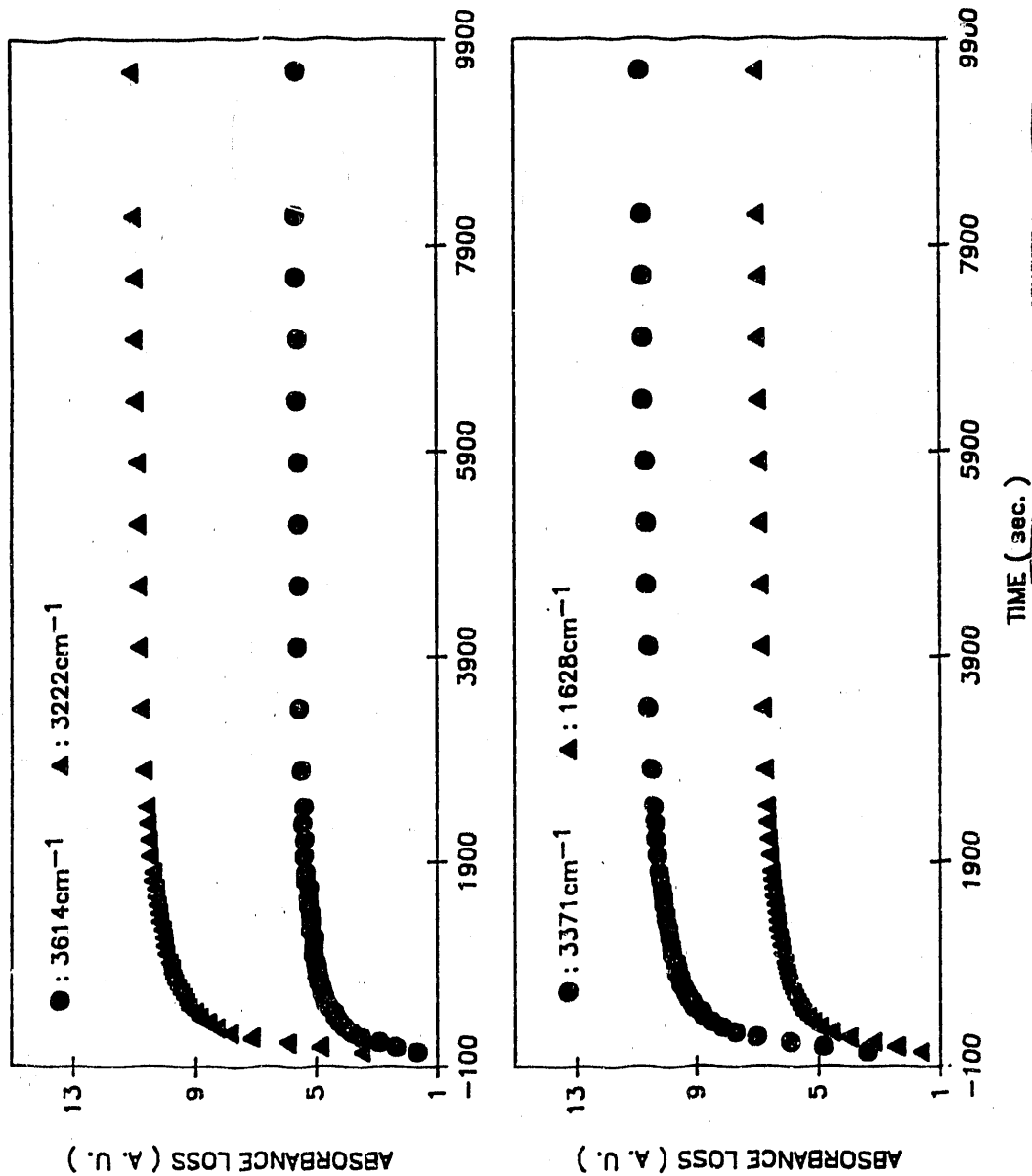


Fig. 5 Isothermal desorption kinetics of 3614, 3371, 3222, and 1628 cm⁻¹ bands measured by monitoring the absorbance loss generated from difference spectrum at (t-0) min.

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