Methane Diffusion Parameters for Sized Coal Particles

A Measuring Apparatus and Some Preliminary Results

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METHANE DIFFUSION PARAMETERS FOR SIZED COAL PARTICLES

A Measuring Apparatus and Some Preliminary Results

by

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ABSTRACT

A sorption apparatus for measuring the equilibrium sorption isotherm and the rate of diffusion of methane from fine-sized coal was designed and constructed. Preliminary work that used Pittsburgh and Pocahontas No. 3 coal shows that the diffusion coefficient varies with pressure and that the fracture spacing in these two coals is substantially different.

INTRODUCTION

Methane gas is formed during the coalification process. Most of it has escaped during this process; however, many coalbeds, especially deeper ones, still retain considerable volumes of the gas. When the coalbed is mined and the methane escapes into the mine workings, those who labor there may be exposed to considerable danger.

The methane in a coalbed often is under considerable pressure. Several hundred pounds per square inch (psi) is common, and pressures as high as 1,000 psi have been measured. Mine workings are, however, at atmospheric pressure, and this difference in pressure causes methane to flow.

The methane present in the coal exists in two states, the "free gas" state and the adsorbed state. The difference between these is that the free gas is compressed in the fractures and macropores of the coal, but the adsorbed gas adheres to the large internal surface that coal is known to have. At normal coalbed pressures, most of the gas is adsorbed. Daines (4)[4] has found that the amount of gas in the adsorbed state at pressures of 300 psi is 10 times as great as the amount of free gas. Bertard, Bruyet, and Gunther (2) have considered the entire volume of gas fixed by coal under stress as being adsorbed. It follows that most of the gas emitted into the mine was adsorbed on the coal originally.

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[3] Physical research scientist.
[4] Underlined numbers in parentheses refer to items in the list of references at the end of the report.

To gain some knowledge about the nature of this emission process, a number of workers have studied the equilibrium sorption isotherm of methane on coal and also the rate of desorption of methane from fine-sized and powdered coal.

SORPTION ISOTHERM

The equilibrium sorption isotherm is the curve relating the quantity of methane adsorbed to the pressure of that quantity; a typical curve for adsorption of dry methane on Pittsburgh-bed coal is shown in figure 1. Most of the recent sorption work on U.S. coals has been done by Ruppel (6), who has determined isotherms for coals of various sizes (up to 1/4-inch) at pressures up to 150 atmospheres.

Desorption From Fine-Sized and Powdered Coal

To understand the sorption rate phenomenon, Hofer, Bayer, and Anderson (5) measured sorption rates on samples of fine-sized Pittsburgh and Pocahontas No. 3 seam coals at near-atmospheric pressure. Among their conclusions were: (1) The rate of sorption is a function of particle size; the rate increases eightfold as the particle size decreases from 6 to 8 mesh to 270 to 325 mesh. (2) The adsorption and desorption curves are identical. (3) The sorption process appears to be diffusion controlled.

Airey (1) did desorption studies using coal samples that ranged in size from 1/2-inch to 200 mesh. He equilibrated his samples at pressures of 50, 150, and 300 psi and then let them desorb at atmospheric pressure. He concluded that the desorption phenomenon could be described by a mathematical model, based on Darcy's law, that incorporated a crack system. The empirical equation he determined was

$$V(t) = A\left[1 - \exp\left\{-\frac{t}{t_0}\right\}^{1/3}\right], \tag{1}$$

where $V(t)$ is the amount desorbed in time t, A is the gas content of the coal, and t_0 is a time constant, with t_0 proportional to mesh size up to 1/4-inch. Airey's results emphasized the importance of studying the desorption of sizes of coal other than powdered.

APPARATUS

An apparatus for measuring equilibrium sorption isotherms and also desorption rates of fine-sized coal was designed and built. Desorption rates can be measured from samples up to 2 inches in size and at pressures up to 1,000 psi.

The apparatus is unique because the pressure changes that occur in the bed pressure as the coal is mined can be simulated. For example, if the coal sample has been equilibrated at 200 psi, the pressure in the sample cylinder can be reduced to 150 psi and held constant at that new pressure while the desorption resulting from that pressure change is measured. The apparatus
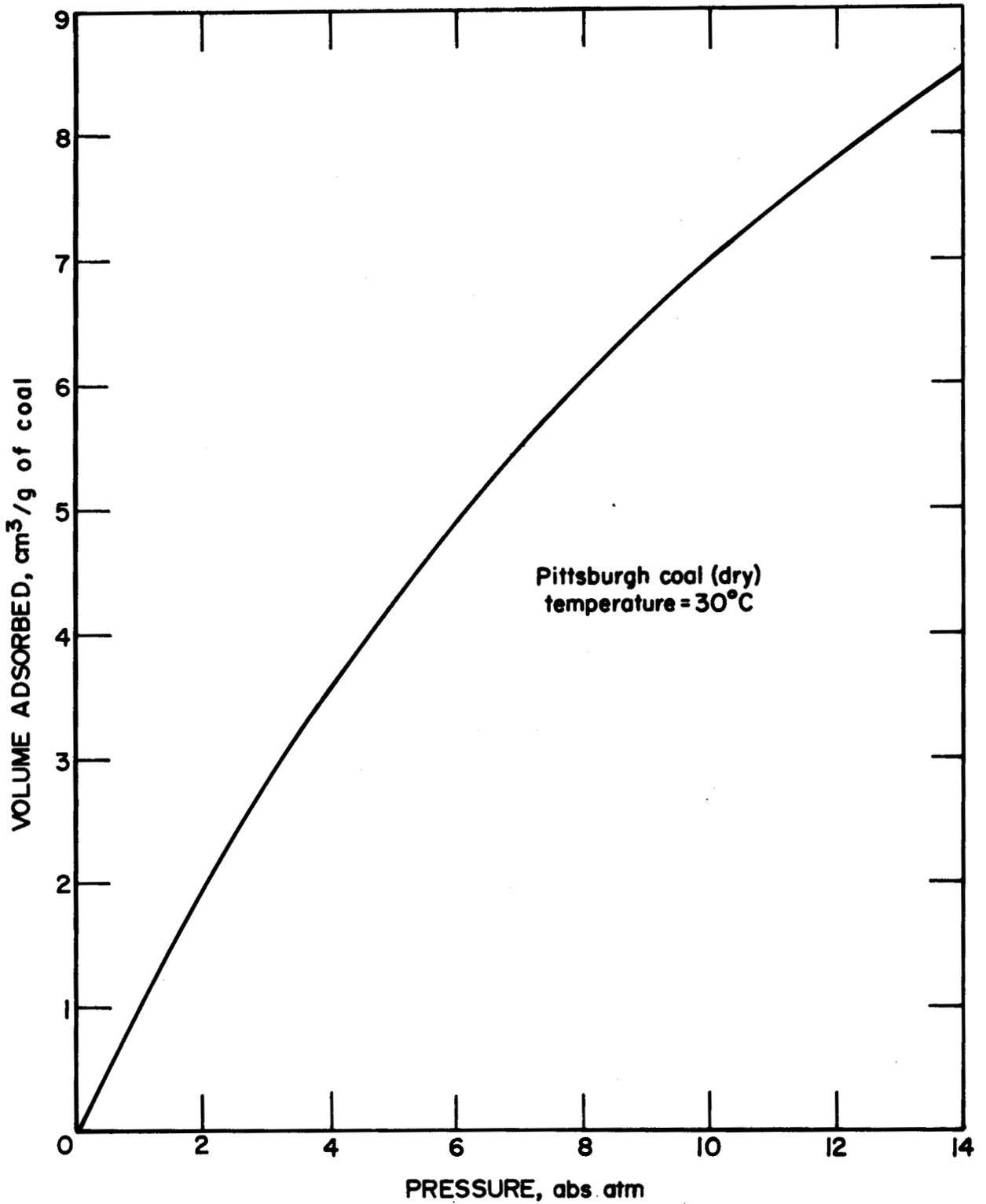
FIGURE 1. - Equilibrium Sorption Isotherm for Methane on Dry Pittsburgh Coal as Derived by Ruppel. The volume was calculated at standard temperature and pressure.
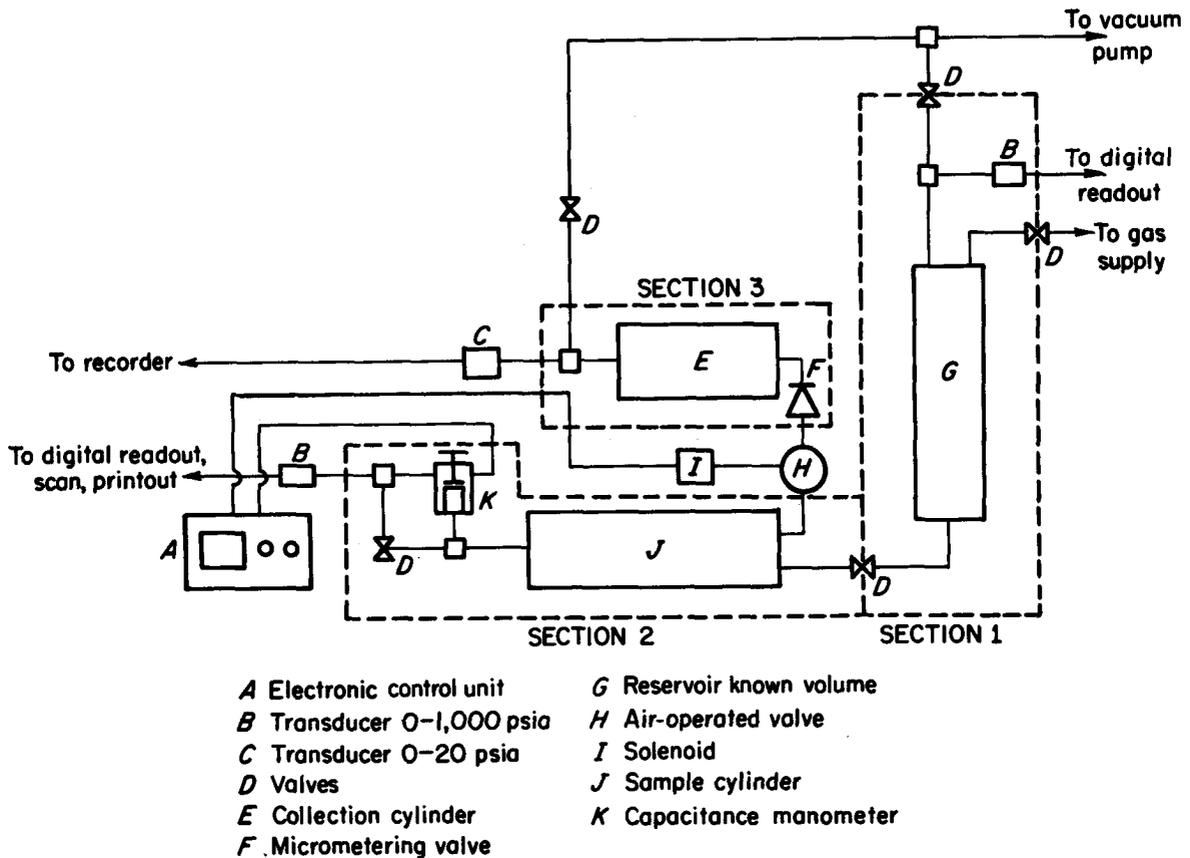
FIGURE 2. - Desorption Apparatus.

A Electronic control unit
B Transducer 0–1,000 psia
C Transducer 0–20 psia
D Valves
E Collection cylinder
F Micrometering valve
G Reservoir known volume
H Air-operated valve
I Solenoid
J Sample cylinder
K Capacitance manometer

consists of three sections (fig. 2): (1) A reservoir cylinder of calibrated volume for measuring the amount of gas used in the experiment; (2) the sample cylinder used to hold the coal sample; and (3) a collecting cylinder where the desorbed gas is collected. Each of these sections can be isolated, and the gas can be retained in the desired cylinder.

To determine the volume of the desorption apparatus, a cylinder of known volume was placed in series with the apparatus. The known-volume cylinder was pressurized with helium while the desorption apparatus was evacuated. The helium was released into the apparatus one section at a time, and the system was tested for leaks with a helium leak detector. The volume of each section was then computed using Boyle's law.

The same procedure, using helium, was followed for determining the free space of the coal-sample cylinder.

In calculating volumes using methane gas, the equation of state for methane was taken as

$$PV = ZnRT, \qquad (2)$$

where P = pressure in atmospheres,

   V = volume in liters,

   Z = the compressibility factor for methane,

   R = the gas constant,

   T = temperature in degrees Kelvin,

and   n = moles.

Although more accurate equations of state are available, this equation gives results that are within experimental error.

To determine the amount of methane adsorbed on the coal, the reservoir cylinder was pressurized with methane. When the temperature in the reservoir cylinder stabilized, the pressure was recorded to determine the number of moles of methane present. The gas then was allowed to flow into the sample cylinder. When the pressure stopped falling noticeably, the sample cylinder and reservoir were again isolated. The remaining number of moles of methane present in the reservoir was subtracted from the initial quantity to determine the number of moles of methane that were introduced into the sample cylinder. The amount of methane adsorbed at any time could be determined by taking the difference between the number of moles in the free space at that time and the number of moles introduced to the sample.

To determine the amount of methane desorbed, the following procedure was followed:

1. The pressure in the sample cylinder was reduced by releasing the gas into the reservoir cylinder.

2. To account for the gas desorbed during step 1, an expected pressure increase in the reservoir cylinder could be determined for a given decrease in pressure in the sample cylinder. The initially desorbing gas causes the pressure in the reservoir cylinder to be greater than the expected pressure, and the amount of initially desorbed gas then can be calculated by taking the difference between these values; that is, actual pressure in the reservoir cylinder minus expected pressure in the reservoir cylinder equals excess pressure resulting from initially desorbed gas.

3. When the pressure in the sample cylinder reached the desired level, the valve leading to the reservoir cylinder was closed.

4. To maintain a constant pressure in the sample cylinder, the excess gas that resulted from desorption was released into the collecting cylinder.

5. Because the volume of the collecting cylinder was known, the amount of gas desorbed could be calculated from the pressure reading in this cylinder.

6. The total amount of desorbed methane could be determined at any time by adding the amount of methane in the collecting cylinder to the amount of methane desorbed during the initial pressure drop.

When desorption rates for low pressures (for example, atmospheric and lower) were measured, it was observed that pressure buildup in the collecting cylinder could retard the flow of gas from the sample cylinder. For this reason, when the pressure in the collecting cylinder was equal to one-half the pressure in the sample cylinder, the collecting cylinder was pumped out, which allowed the gas that resulted from desorption to flow freely into the collecting cylinder.

As mentioned previously, the unique feature about this apparatus is that it can measure desorption rates from coal samples incrementally at elevated pressures while holding the gas pressure over the coal sample constant. This is accomplished by using a capacitance manometer to monitor the pressure in the sample cylinder. Essentially, the capacitance manometer is a sensitive differential pressure transducer capable of measuring pressure changes of less than 0.01 psi at a pressure of 300 psia. With a small pressure change, an air-operated valve controlled by the capacitance manometer is activated. This allows the excess desorbed gas to flow through a micrometering valve into a collecting cylinder. When the excess gas, equal in amount to the gas desorbed, has been released from the sample cylinder, the capacitance manometer senses the drop in pressure and closes the air-operating valve. The result is that it is possible to desorb a sample at a series of intermediate pressures that are held constant, rather than just reducing the pressure from some initial value to atmospheric.

SAMPLE PREPARATION

Coal for each sample to be tested was crushed to 1- by 1/2-inch size, screened, and then floated in carbon tetrachloride to remove foreign mineral matter. The cleaned samples were dried in a vacuum oven at 100° C for about 24 hours. The dried coal was weighed and put into the sample cylinder. The coal was reheated to approximately 70° C, in the sampling cylinder under vacuum, to insure the removal of air and moisture that may have been adsorbed while loading into the cylinder. The reheating process was repeated until the pressure in the cylinder stabilized.

RESULTS

For these preliminary experiments the importance of two factors on the desorption rate had to be determined: The effect of total pressure and the effect of particle size.

Effect of Total Pressure

Airey (1) has desorbed coal from initial pressures of 50, 100, and 150 psi to atmospheric pressure. However, a more sensitive method of assessing whether a pressure effect exists is to desorb to a series of intermediate pressures. This was done on two types of coal, 180- to 200-mesh Pittsburgh coal and 1/2- to 1/4-inch Pocahontas No. 3 coal.
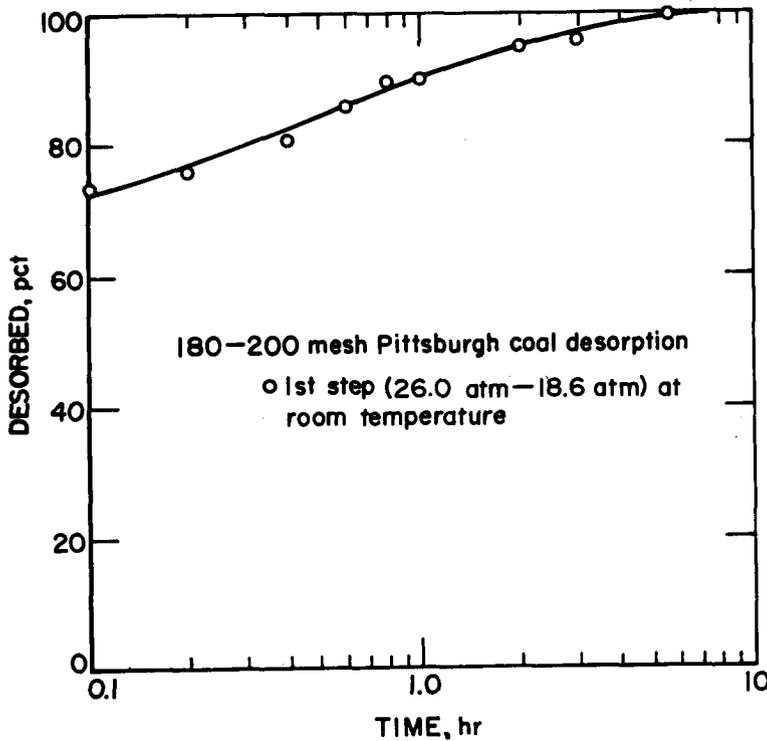
FIGURE 3. - Typical Desorption Curve for 180- to 200-Mesh Pittsburgh Coal.

Pittsburgh Coal

The Pittsburgh coal was pressurized to 26.0 atmospheres, and after equilibrium was achieved, the pressure was reduced to 3.9 atmospheres in five stages. The stages are shown in table 1, and a typical desorption curve for this sample is shown in figure 3.[5]

Table 1 gives the initial and final pressures for each desorption step, the amount of gas desorbed in each step, the time required for 75 percent of the desorption to take place, and the diffusion parameter D/a^2. It shows that as the pressure decreases the desorption time increases. If methane is escaping from this fine powder by a diffusion-controlled process, it follows that the diffusion parameter is decreasing as the pressure falls.

TABLE 1. - Five-step desorption on 180- to 200-mesh size Pittsburgh coal

Step	Starting pressure, atm	Final pressure, atm	CH_4 desorbed, cm^3/g (1 cm^3/g = 32 ft^3/ton)	Time for 75-pct desorption, min	D/a^2, sec^{-1}
1	26.0	18.6	2.28	10	1.55×10^{-4}
2	18.6	13.9	1.69	14	1.11×10^{-4}
3	13.9	9.1	1.80	18	$.86 \times 10^{-4}$
4	9.1	6.3	1.31	21	$.74 \times 10^{-4}$
5	6.3	3.9	1.38	45	$.34 \times 10^{-4}$

Pocahontas Coal

The Pocahontas coal was pressurized initially to 21.4 atmospheres and then desorbed in three stages. Table 2 gives these quantities and also the time for 25-percent desorption. This 25-percent figure is available because the rate of emission from the Pocahontas lumps was much slower than it was for

[5] All of the desorption curves for coal were obtained at room temperature.

the Pittsburgh coal powder. Emission rate curves for all three steps are given in figure 4.

TABLE 2. - Three-step desorption on 1/2- to 1/4-inch Pocahontas No. 3 coal

Step	Starting pressure, atm	Final pressure, atm	CH_4 desorbed, cm^3/g (1 cm^3/g = 32 ft^3/ton)	Time for 25-pct desorption, min	D/a^2, sec^{-1}
1	21.4	6.67	5.1	144	5.8×10^{-7}
2	6.67	2.23	3.8	245	3.5×10^{-7}
3	2.23	.88	2.4	288	2.5×10^{-7}

In both tables the diffusion parameter D/a^2 is obtained from a solution to the diffusion equation, valid for spherical particles:

$$\frac{Mt}{M\infty} = 6 \left(\frac{Dt}{a^2} \right)^{1/2} \left\{ \pi^{1/2} + 2 \sum_{n=1}^{\infty} i^` erfc \frac{na}{\sqrt{Dt}} \right\} -3 \frac{Dt}{a^2} . \tag{3}$$

Here, $Mt/M\infty$ is the fraction desorbed at time t (seconds), D is the diffusion parameter $\left(\frac{centimeters^2}{seconds} \right)$ and a is the sphere radius (centimeters). This solution may be written in terms of the dimensionless parameter Dt/a^2, and Dt/a^2 versus $Mt/M\infty$ is presented graphically in a publication by Crank (3).

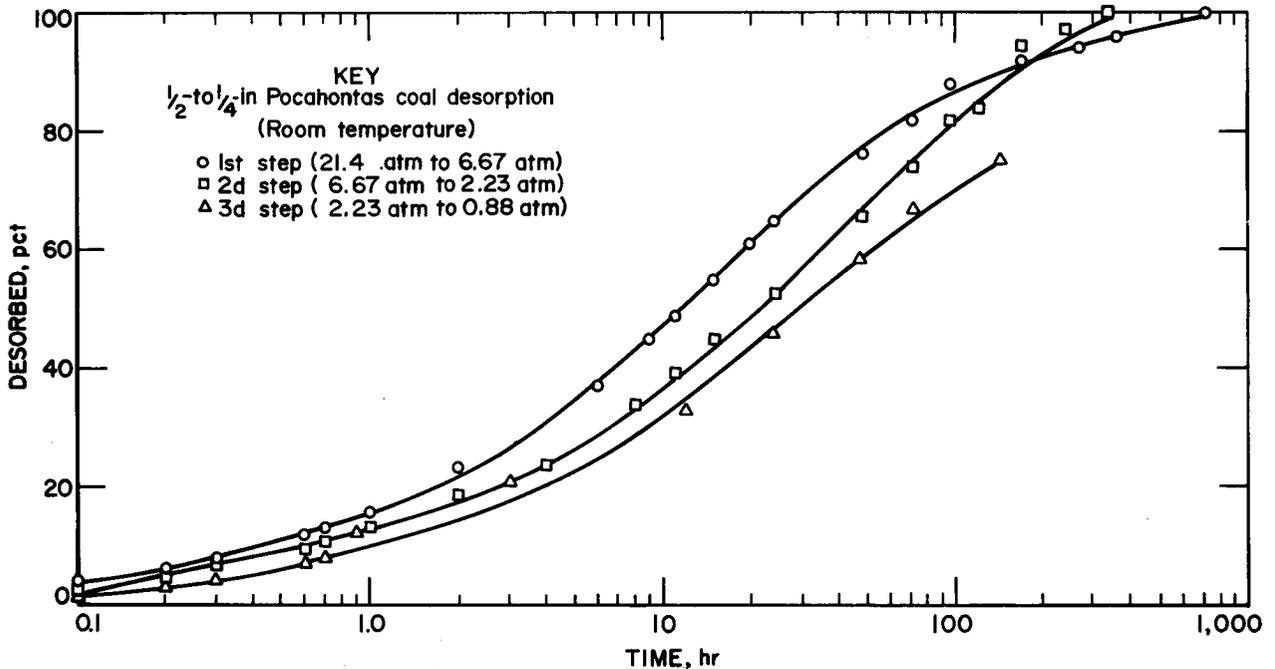FIGURE 4. - Three-Stage Desorption for ½- to ¼-Inch Pocahontas No. 3 Coal.

In both cases, the diffusion parameter shows the anticipated decrease as the pressure falls. It appears that the decrease in the diffusion parameter is less for the Pocahontas coal than for the Pittsburgh coal; however, the first desorption step for the Pocahontas coal is very large compared with that of the Pittsburgh coal, and the value of 5.8×10^{-7} must be regarded as an average over many smaller steps.

Hofer, Bayer, and Anderson (5) have also obtained diffusion parameters for these same coals. For 270- to 325-mesh Pittsburgh coal they got a D/a^2 of 1.16×10^{-4} sec^{-1}, and for 6- to 8-mesh Pocahontas coal, a D/a^2 of 5.9×10^{-6} sec^{-1}. However, they did not note a pressure effect on the rate of sorption.

Effect of Size

Bertard and others (2) have claimed that when the dimensions of a piece of coal exceed the fissuring network, the desorption rate will be practically independent of size distribution. They also claim that the fissuring network generally does not exceed 1 millimeter. This was found to be true for the Pocahontas No. 3 coal, but for the Pittsburgh coal the fissuring network was 1/2-inch or more.

Pocahontas No. 3 Coal

Desorption curves for Pocahontas No. 3 coal in three size ranges are shown in figure 5. It may be seen that there is very little difference in the desorption curves for 1/16- to 1/32-inch and 1/2- to 1/4-inch size coals and that 20 to 65 mesh (approximately 1/32- to 1/128-inch) desorbs slightly
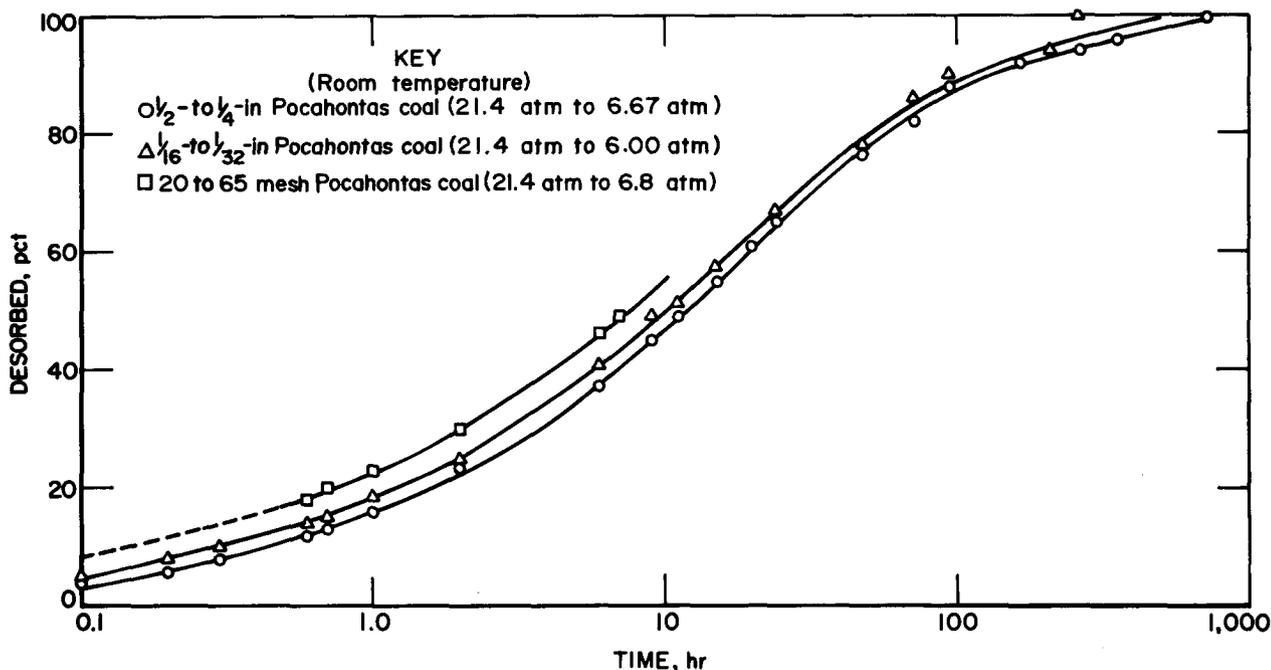

FIGURE 5. - Desorption Curves for Three Sizes of Pocahontas No. 3 Coal.

faster. The spacing of the fissure network is 1/16-inch or less, in agreement. with the results of Bertard and others.

Precautions were taken to insure that the samples were fully equilibrated before they were desorbed. The apparatus is designed so that adsorption curve data may be calculated for each sample. This is used to insure that the sample is fully equilibrated. A typical adsorption curve is shown in figure 6. This particular sample, 1/16- to 1/32-inch, required 3 weeks to fully equilibrate, and it adsorbed 15.1 cubic centimeters per gram at 21.4 atmospheres pressure. If all the samples of this coal are fully equilibrated, they will adsorb the same amount of gas at a given pressure. The 1/2- to 1/4-inch and 20- to 65-mesh samples also were pressurized to the same initial pressure, 21.4 atmospheres, and each adsorbed about 15 cubic centimeters per gram of methane, which showed that they were properly equilibrated.

Pittsburgh Coal

Desorption curves for 1/16- to 1/32-inch and 1/2- to 1/4-inch Pittsburgh coal are shown in figure 7. As with the Pocahontas coal, both samples were allowed to equilibrate before desorbing, although this required several months. An attempt was made to test Pittsburgh coal in the size range 1- to 1/2-inch, but in 9 months this sample had not reached adsorption equilibrium, and it was discarded.

It is evident from figure 7 and also from the very slow adsorption on 1- to 1/2-inch coal that even the 1/2- to 1/4-inch size was less than the fissure spacing.
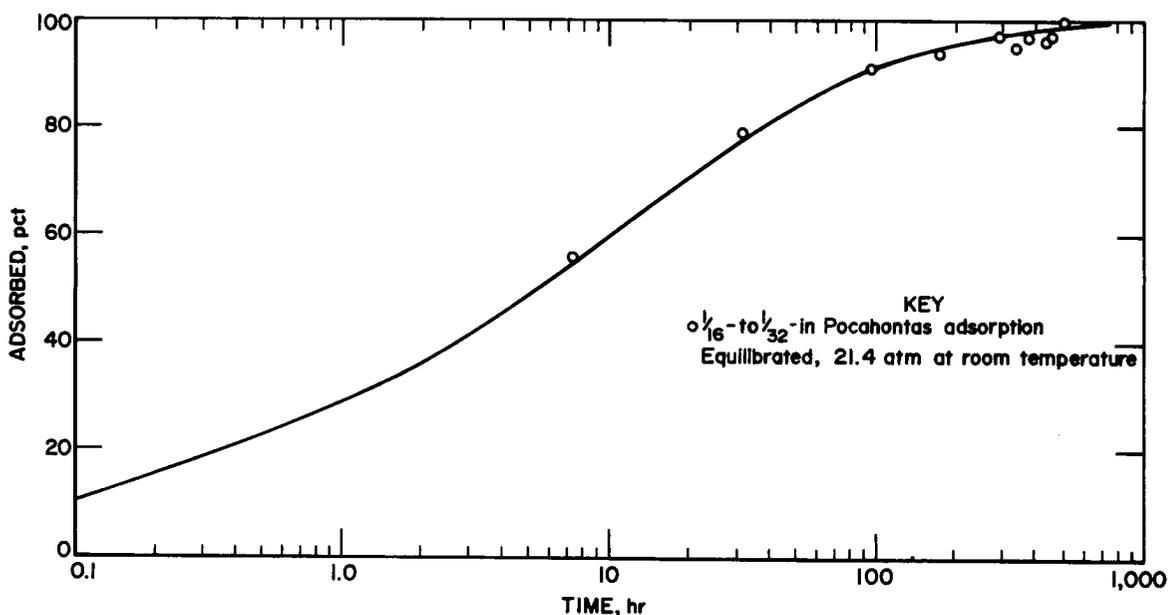

FIGURE 6. - A Typical Adsorption Curve for Pocahontas No. 3 Coal.
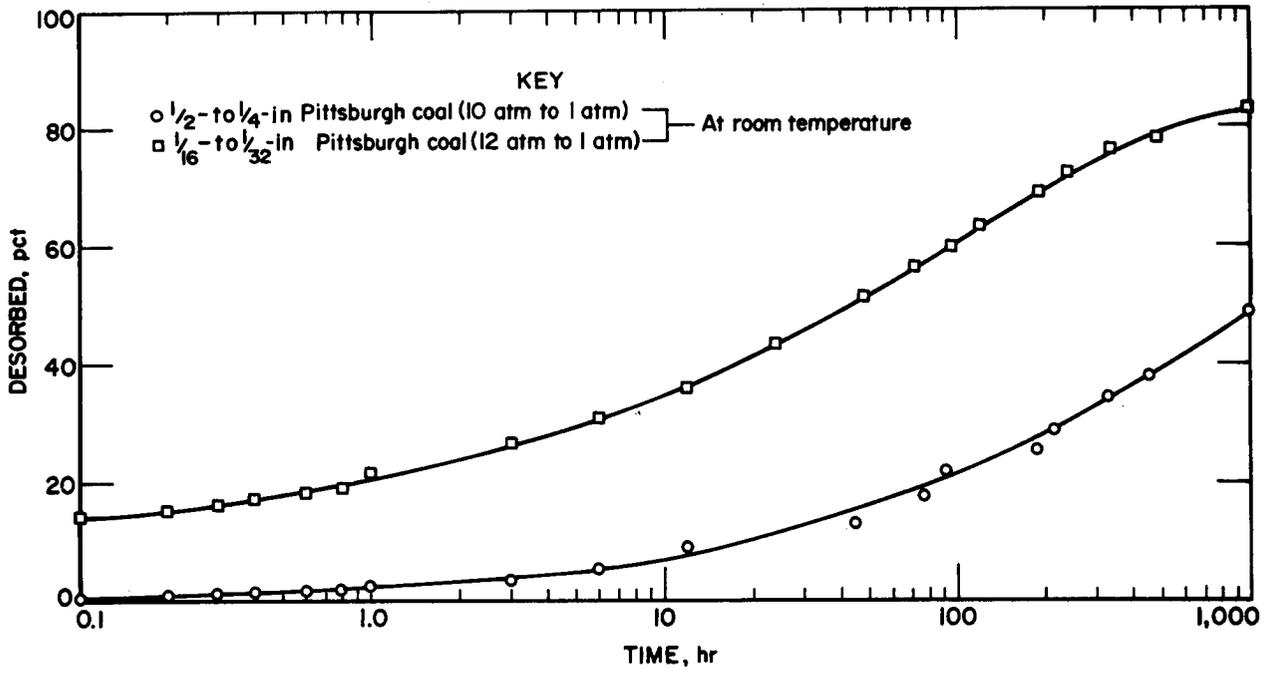
FIGURE 7. - Desorption Curves for Two Sizes of Pittsburgh Coal.

CONCLUSIONS

1. An apparatus for measuring adsorption and desorption rate curves for methane on fine-sized coal was designed and constructed.

2. The unique feature of this apparatus is that the coal samples may be desorbed at intermediate pressures that are held constant.

3. The diffusion parameter varies with pressure in both Pittsburgh and Pocahontas No. 3 coals, and decreases as the pressure decreases.

4. The spacing of the fissure network in Pocahontas No. 3 coal is 1/16-inch or less, whereas in the Pittsburgh coal it is 1/2-inch or more.

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