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AN EVALUATION AND COMPARISON  
OF DIFFUSION STUDIES

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## AN EVALUATION AND COMPARISON OF DIFFUSION STUDIES

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### ABSTRACT

The Eastern Gas Shales Project had four contractors engaged in diffusion or permeation tests on Devonian shales. Alfred University and Battelle Labs have completed their studies. Those of Juniata College and Mound Facilities are continuing. These studies were compared to tests run at METC during 1977.

A formula was developed at METC to convert diffusivities ( $\text{cm}^2/\text{sec}$ ) to permeabilities ( $\text{cm}^2$ ). In this conversion, it was necessary to know the temperature and pressure of each experiment.

The results were remarkably similar considering the different methods that were used. Juniata College used sorption methods while the other labs were involved with flow-through methods of different types. With the exception of Alfred's data, all the values were similar, with the averages ranging from  $0.10 \times 10^{-8}$  to  $0.02 \times 10^{-8}$  darcys for permeation perpendicular to bedding planes.

The desorption method of Juniata College probably most accurately describes the diffusion of gas into a fracture system connected to the well bore. Flow-through methods probably best describe those wells with large pressure differences in the beginnings of production.

### INTRODUCTION

The report is a comparison of the results of the work of contractors that have completed diffusion tests for the Eastern Gas Shales Program (EGSP). Alfred University completed their work in September, 1977 and Battelle Labs completed theirs in February, 1978. Juniata College is continuing its diffusion studies. Mound Facilities started their program in March, 1978.

Secondly, the report is an evaluation of the procedures of each contractor and what effect these procedures have on the data. In order to evaluate the data, the experimental and analytical method must be known. A description of each experimental procedure and the analysis for the calculations is given in sufficient detail to show the logic of each process.

## INTRODUCTION (Cont.)

Sources of information were the monthly and quarterly reports prepared for the EGSP and conversations with the various experimenters.

## DESCRIPTION OF EXPERIMENTAL AND ANALYTICAL METHODS

This section is a detailed description of the methods of each laboratory. The description is divided into two parts, the experimental and the analytical.

Juniata made use of a desorption method. All the other labs used flow-through methods. Juniata, METC and Mound used methane gas while Battelle used helium and Alfred used air as the permeating medium. Actual shale samples were used in all cases, either powder or slabs. The slabs were oriented parallel and perpendicular to bedding.

### DIFFUSION EXPERIMENTS OF MOUND FACILITY

#### Experimental Procedure

The Mound Lab experiments started in March, 1978. Their method was to pressurize one side of a rock sample and keep a low pressure on the opposite side (19). A record was kept of the amount of gas lost on the high pressure side (20).

The experimental apparatus was modified to monitor the concentration of gas on the low pressure side by a manometer rather than by mass spectrometry. This arrangement is similar to that of Battelle Labs to measure the amount of gas lost from the high pressure reservoir.

The sample was sealed using two O-rings and a plastic sleeve. With the sample in place, a vacuum was maintained on both sides of the sample in order to seal the sides with plastic. Methane and other gases naturally occurring within the shale as well as mixtures of these gases, were used as diffusing gases.

#### Analytical Method

Mound Labs determined the permeability of shale based on Darcy's law (20). This law is an empirical relationship of the properties of the porous solid and the gas (6, pp. 47-51).

The statement of this law for incompressible fluids is

$$q = \frac{KA}{\mu L} (P_a - P_b)$$

where  $q$  is the volumetric flow rate,

$K$  is permeability having units of length squared,

$A$  and  $L$  are dimensions of the solid (area and length),

$\mu$  is viscosity of the fluid,

$P_a$  and  $P_b$  are the high pressure and low pressure sides of the sample

ANALYTICAL METHOD (Cont.)

respectively.

For horizontal linear flow, gravitational parameters have no effect and, therefore, are not included in the equations.

Equation 1 is valid for gases provided  $q$  is defined as the volumetric flow rate ( $\bar{q}$ ) which is measured at the mean pressure,  $\frac{P_a + P_b}{2}$ . For an ideal gas

$$\underline{2} \quad \bar{q} \left( \frac{P_a + P_b}{2} \right) = q_a P_a, \text{ where } q_a \text{ is the}$$

flow rate measured at any pressure  $P_a$ . Combining equation 1 and 2 gives Darcy's law for an ideal gas.

$$\underline{3} \quad q_a P_a = \frac{KA}{2\mu L} (P_a^2 - P_b^2)$$

Because real gases do not adhere to the pore walls as would be required for laminar flow, a correction is necessary. Real gases possess slip, and this slippage of the gas along the pore walls gives rise to an apparent dependence of permeability on pressure, the Klinkenberg effect (6, p. 51).

$$\underline{4} \quad K = K_\infty \left( 1 + \frac{b}{P} \right) = K_\infty \left( 1 + \frac{2b}{P_a + P_b} \right), \text{ where}$$

$K_\infty$  is permeability for an incompressible fluid, and  $P$  is the mean flowing pressure.  
 $b$  is a constant dependent on the gas and solid.

For high pressure gas flow, slip can be neglected because at high pressure the gas molecules effectively adhere to the pore walls, and equation 3 may be used with  $K$  replaced by  $K_\infty$ .

$$\underline{5} \quad q_a P_a = \frac{K_\infty A}{2\mu L} (P_a^2 - P_b^2)$$

For low pressure gas flow, slip flow cannot be neglected and the required relationship is found by combining equation 3 and 4 to give Darcy's law for real gases.

$$\underline{6} \quad q_a P_a = \frac{K_\infty A}{2\mu L} \left( 1 + \frac{2b}{P_a + P_b} \right) (P_a^2 - P_b^2)$$

Under actual experimental conditions, the incompressible fluid permeability ( $K_\infty$ ) is calculated. For liquids, a single measurement gives  $K$  directly through equation 1. For an ideal gas and real gases at high pressures, a single measurement gives  $K$  directly through equations 3 and 5. For real gases at low pressures, measurements at several mean pressures are necessary because  $b$  in equation 6 is not generally known. Permeabilities are

## ANALYTICAL METHOD (Cont.)

calculated at any given pressure,  $P_a$ , by using equation 3. These permeabilities are plotted against the inverse of the mean pressures (equation 4) and  $P_\infty$  is found as the intercept.

At very low pressures, diffusion occurs as opposed to flowage. As their experimental program proceeds and if it is found that diffusion rather than flowage is occurring, then the appropriate diffusion equations will be used (20).

## DIFFUSION EXPERIMENTS OF BATTELLE LABS

### Experimental Procedure

The experimental procedure was a modified steady state method (4, p. 844). A cold trap and roughing pump maintained a vacuum (100 microns) on one side of a shale slab (8). The pressure on the other side of the slab was slightly greater than atmospheric. This pressure decreased during the time of the experiment to atmospheric pressure. All tests were run at room temperature.

At the start of the experiments, helium was added to the manometer. The fall of mercury in the open manometer arm was a measure of the amount of gas permeated.

The volume of the specimen holder was subtracted from the total gas permeated. This was done by inserting a nonporous plug into the cell and measuring the rise in the manometer to a constant value.

### Analytical Method

A permeability constant was derived through calculations based on Darcy's Law.

The steady state equation is

$$K = \frac{Q \mu L}{A(P_1 - P_2)},$$

where  $\mu$  is viscosity of He gas at room temperature, and

$A L$  is the volume of the shale (area times length),

$Q$  is the gas permeated per unit time and,

$P_1 - P_2$  is pressure difference across length  $L$  of the solid.

$K$  has units of darcys when  $Q$  is in cc/sec,  $\mu$  in centipoise,  $L$  in cm.,  $A$  in cm.<sup>2</sup>, and  $(P_1 - P_2)$  is in atmospheres.

## DIFFUSION STUDIES AT ALFRED UNIVERSITY

### Experimental Procedure

The experimental apparatus has previously been described by W. E. Brownell in "Procedures for the Characterization of Devonian Shales," First Eastern Gas Shales Symposium, October 17-19, 1977, pp. 501-508. This procedure was similar to that of Schumacher and Ferguson (19) but without evacuation of air.

The apparatus consisted of a sealed chamber containing the rock sample. On one side of the sample air pressure was maintained at 60 psi. An oil manometer on the low pressure side measured the gas flow. The low pressure side was at atmospheric pressure initially. As permeation continued, the backpressure increased as a result of the displaced oil column. Duration of a typical test was about one hour.

### Analytical Method

The mathematical calculations were briefly discussed in EGSP Report No. 18 (2). The experimental procedure involved a backpressure buildup on the manometer as permeation continued. The calculations were based on the work of Muskat (11,12).

An equation is derived from Darcy's Law applicable to compressible fluids such as gases. Instantaneous steady-state flow conditions are assumed in the development of the equation. It is also assumed that Darcy's Law is obeyed, i.e. flow is in the viscous range. As permeation continues, there is a pressure rise in the apparatus. This change in pressure (P) with a change in the volume of air passed (V), as a function of time, is

$$P = P_i + aV$$

where  $P_i$  is the initial pressure and "a" is a constant dependent on the geometry of the apparatus and has units of pressure per unit volume.

An appropriate analytical relationship is established by assuming that the fluid pressure rises from its initial value and continually increases the back-pressure on the sample.

This back-pressure ( $aV$ ) is equal to the following relationship.

$$aV = (P_e - P_i) \left( 1 - \exp\left(-\frac{\gamma g c t}{\alpha}\right) \right), \text{ where}$$

$P_e$  is final equilibrium pressure, and  
 $\alpha$  = the area of the manometer.

$c = \frac{KA}{\mu L}$ , where c is a constant, and K is the permeability of the sample and  $\mu$  is the viscosity of the gas;

A is area of the sample,

L is thickness of the sample,

$\gamma$  is average density of the gas permeated, and

g is the acceleration due to gravity.

### ANALYTICAL METHOD (Cont.)

Rewriting equation 1,

$$\underline{2} \quad \ln \frac{P_e - P}{P_e - P_i} = - \frac{\gamma g c t}{\alpha}$$

Making the appropriate substitutions for  $c$  and solving equation 2 for  $K$  gives

$$\underline{3} \quad K = - \frac{\alpha \mu L}{\gamma g A t} \ln \left( \frac{P_e - P_i - aV}{P_e - P_i} \right)$$

Specifically for the Alfred apparatus, the following value was determined.

$$\frac{\alpha}{\gamma g} = \frac{0.2449}{a}, \text{ assuming } \gamma \text{ constant.}$$

$P_r$  and  $P_o$  are not defined in the original Alfred report but are assumed to be equal respectively to  $P_e$  and  $P_i$ .

Finally,  $K$  in millidarcys is given by

$$\underline{4} \quad K = - \frac{0.2449 \mu L}{a A t} \ln \left( 1 - \frac{a V}{P_r - P_o} \right)$$

The following values were determined for  $a$  and  $A$ .

$a = 0.0694$  psi/ml, an empirical constant dependent on the Alfred apparatus.

$A = 330$  mm<sup>2</sup> for the Alfred samples.

### DIFFUSION EXPERIMENTS AT METC

#### Experimental Procedure

The experimental procedure involved gas flow through a solid membrane from a high pressure source (7). The gas was held at a constant pressure, usually seven atmospheres, on one side of a shale slab. The pressure build-up on the low-pressure side of the slab was measured with a mercury manometer. A single test lasted approximately four (4) weeks.

The samples were cut from a 4-inch core using a one-inch diameter diamond bit. The ends were then machined parallel on a lathe. An average slab was 2.5 cm across and 0.9 cm thick. The samples were dried in a desiccator and then cemented into a stainless steel flange with epoxy.

Industrially pure methane was used on the high pressure side. When the pressure had been built up to a constant value, measurements of time, temperature and pressure began. Atmospheric pressure was measured with a mercury barometer. The gauge pressure on the low pressure side was measured by the mercury manometer. The total low pressure chamber pressure was the sum of the manometer and barometric pressures.

## EXPERIMENTAL PROCEDURE (Cont.)

Data included pressure buildup with time and the calculated moles diffused with time. Least squares trend lines were found for this data. From these trend lines the initial pressure, the final pressure and the number of moles permeated were determined.

The methane equation of state was used to calculate the gas concentrations (1). This cubic equation was solved by computer.

### Analytical Method

The method is based on that of Paul and DiBenedetto (13). A solution for the analogous problem of heat flow is found in Carslaw and Jaeger (5, pp. 128-129).

The initial concentration within the solid is  $C_{Li}$ . One face of the solid is in contact with gas at a pressure of  $P_H$ . The surface of the solid is at a concentration  $C_H = SP_H$ , where  $S$  is the solubility of gas in the solid. At the opposite face, the solid is in contact with gas at a pressure of  $P_{Li}$  initially, where  $C_{Li} = SP_{Li}$ .

The change in concentration with the solid is then

$$\frac{1}{C_H - C_{Li}} \frac{C - C_{Li}}{C_H - C_{Li}} = 1 - \sum_{k=0}^{\infty} \frac{2(\beta_k^2 + \eta^2) \sin \beta_k \frac{x}{L}}{\beta_k (\beta_k^2 + \eta^2 + \eta)} \exp \frac{-D\beta_k^2 t}{L^2}$$

where  $\beta_k$ s are positive roots of  $\beta \tan \beta = \eta$ .

The most easily measured quantity is the amount of gas permeated through the shale in time  $t$  ( $Q$  in moles) and related to the diffusion parameter by the following equation.

$$\frac{2}{L} Q = \int_0^t N \Big|_{x=1} dt = A \int_0^t \left( -D \frac{\partial C}{\partial x} \Big|_{x=1} \right) dt$$

The solution of  $\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$  with

conditions  $C_{Li} = SP_{Li}$  at  $0 \leq x \leq 1$  when  $t < 0$

$C_H = SP_H$  at  $x = 0$  when  $t \geq 0$

$C_L = SP_L$  at  $x = 1$  when  $t \geq 0$

is obtained by combining equations 1 and 2.

$$\frac{3}{L} Q = ALS' (P_H - P_{Li}) \sum_{k=0}^{\infty} Ak - \sum_{k=0}^{\infty} Ak \exp \frac{-\beta_k^2 Dt}{L^2}$$

$$\text{with } Ak = \frac{2(\beta_k^2 + \eta^2) \cos \beta_k}{\beta_k^2 (\beta_k^2 + \eta^2 + \eta)}$$

$\eta$  is a constant determined from experimental parameters and is equal to

$$\eta = \frac{SALP' P_{Lf}}{QRT}$$

ANALYTICAL METHOD (Cont.)

Q is the number of moles of gas permeated in time t,  
AL is the volume of solid in cm<sup>3</sup> (area times length),

R is the gas constant,  $82.056 \frac{\text{cc} \cdot \text{atm}}{\text{mole} \cdot \text{K}}$

T is the average temperature in degrees Kelvin,

S is gas solubility in the shale, given as 0.252 cc gas/cc rock · atm,

S' is gas solubility in the shale, given as  $1.11 \times 10^{-5}$  moles gas/cc  
rock · atm,

P<sup>1</sup> is the partial pressure of gas permeated in atmospheres,

P<sub>Lf</sub> is final pressure of gas on low pressure side of solid in atmospheres.

The solubility was determined from data gathered by Juniata College (18, p. C5). Paul Schettler found that the S values were in a narrow range for most shale samples. The values used above are average values based on his work.

In order to find D, the diffusion coefficient, the following procedure was used:

The value of β<sub>0</sub> was determined. β<sub>0</sub> is an angle based on the equation β tan β = η. Next, A<sub>0</sub> another constant based on β<sub>0</sub> and η was found. The computer found values for β<sub>1</sub> up to β<sub>200</sub> and summed the terms. Two hundred terms were found to be sufficient to give a constant value for the summation to 4 to 5 decimal places.

The computer, using values of  $\sum_{k=1}^{\infty} A_k$ , A<sub>0</sub> and the experimental product value  $\frac{Q}{ALS(P_H - P_{Li})}$ , found the value of the constant Dt/L<sup>2</sup>.

Knowing the length of time of the experiment and the thickness of the slab, D was calculated.

DIFFUSION EXPERIMENTS OF JUNIATA COLLEGEExperimental Procedure for Particles

The initial work in 1976 involved nitrogen adsorption at 77°K and methane desorption at 0°C. Since October 1977, all work has been methane desorption.

Samples taken from the core were ground, made dust free and the weights recorded. The procedures have been standardized to those that were found to disturb the shale samples the least. Therefore, beginning in June 1977, all samples were ground on a percussion mortar to a size range of 500-700 microns.

Sieved samples were placed in a pyrex cell which was then attached to the system by glassblowing (15). Samples were evacuated for a few minutes, then placed under an atmosphere of pure methane. A run was started after equilibrium had been attained, which usually occurred in 15 minutes. After the equilibrium pressure (P<sub>s</sub>) was measured; the computer automatically collected pressure readings. The pressure was

## EXPERIMENTAL PROCEDURE FOR PARTICLES (Cont.)

decreased suddenly from the equilibrium pressure, and the new pressure ( $P_0$ ) and time zero were found.

$P_s$  was typically 900 torr and  $P_0$  about 150 torr. The computer continued to collect pressure data as degassing proceeded until the pressure became constant at some value slightly above  $P_0$ . This final, constant pressure was symbolized by  $P_\infty$ . The length of time required for degassing was about 15 minutes. The program calculated  $\alpha$ ,  $D$  and compared  $D$  to the general function.

Specific degasibility was calculated after finding the volume and temperature of all parts of the system (18).

### Experimental Procedure for Slabs

Samples were cut on a diamond saw with water lubricant and dried (16). All surfaces except the sorption face were coated with epoxy glue and aluminum foil was layered onto the wet epoxy glue. After the glue dried, the shale surfaces were shaved down with a chisel.

The shale faces were traced onto graph paper and the total area was measured by planimeter. Samples were then sealed in the cell by glass-blowing. The slabs required equilibration over several days in a methane atmosphere in contrast to particles which equilibrated in a few minutes.

Procedures were the same as for meshed particles except for the following differences:

$P_s$  was typically 750 torr and  $P_0$  about 400 torr. From zero time to the end of the run was usually 30 minutes in contrast to particles.  $P_\infty$  for slabs would have been in the range of days or weeks. In order to get around this problem of the long time to determine  $P_\infty$ , separate isotherm data was obtained from particles sampled from the same depth as the slabs.

The volumes of the system and of the sample cell were determined. Computer software has been developed to find all these values.

Specific degasibility does not require a solubility constant from particles. Thus, it is calculated directly from data in the program (18).

## ANALYTICAL METHOD FOR PARTICLES

The general solution for the problem of sorption from particles assumed to be uniform spheres, is given by Crank (7, pp. 93-96). Initially, all spheres are assumed to contain solute at a uniform concentration,  $C_0$ , and the fluid to be solute free. A solution of the diffusion equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}, \text{ is required.}$$

ANALYTICAL METHOD FOR PARTICLES (Cont.)

A general solution of this diffusion equation in a form expressing the total amount of solute desorbing from the spheres up to time  $t$  ( $M_t$ ) as a fraction of the corresponding amount after the infinite time ( $M_\infty$ ) is

$$1 \quad \frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6 \alpha (\alpha+1) \exp(-Dq_n^2 t/a^2)}{9 + 9\alpha + q_n^2 \alpha^2}$$

where  $q_n$ 's are the non-zero roots of

$$\tan q_n = \frac{3 q_n}{3 + \alpha q_n^2}$$

and  $\alpha = \frac{3V}{4\pi a^3 S}$  where  $S$  is the solubility factor of gas in the solid,  $a$  is the radius of the spheres, and  $V$  is the volume of the space surrounding the spheres.

For short times (less than one day), the general solution is difficult to evaluate. This is because the smaller  $\frac{Dt}{L^2}$  is, the more terms in the series are needed for a given accuracy. Carman and Haul (3) give an alternative solution for small times appropriate for most experimental setups. The short time solution is again given in terms of a ratio of the amount of solute desorbed from the spheres in time  $t$  ( $M_t$ ) to the corresponding quantity after infinite time ( $M_\infty$ ).

$$2 \quad \frac{M_t}{M_\infty} = (1+\alpha) \left[ 1 - \frac{\gamma_1}{\gamma_1 + \gamma_2} e \operatorname{erfc} \left\{ \frac{3\gamma_1}{\alpha} (B)^{1/2} \right\} - \frac{\gamma_2}{\gamma_1 + \gamma_2} e \operatorname{erfc} \left\{ -\frac{3\gamma_2}{\alpha} (B)^{1/2} \right\} \right]$$

$$\text{where } B = \frac{Dt}{a^2}, \text{ and} \quad \gamma_1 = \frac{1}{2} \left\{ \left( 1 + \frac{4}{3}\alpha \right)^{1/2} + 1 \right\}$$

$$\gamma_2 = \gamma_1 - 1$$

The particle radius is  $a$  and the function  $e \operatorname{erfc} z$  is defined as  $\exp z^2 \operatorname{erfc} z$  (3, p. 112). The higher terms may be neglected as their overall effect is negligible.

For the smallest values of  $B$  (i.e. short times), equation 1 can be expanded into a series as follows.

$$3 \quad \frac{M_t}{M_\infty} = (1+\alpha) \left[ \frac{6}{\alpha} \left( \frac{B}{\pi} \right)^{1/2} - \left( 1 + \frac{\alpha}{3} \right) \frac{9B}{\alpha^2} + \left( 1 + \frac{2\alpha}{3} \right) \frac{36}{\alpha^3} \left( \frac{B^{3/2}}{\alpha^3} \right) + \dots \right]$$

Only the first term needs to be considered for the initial slope of the above equation.

$$4 \quad \frac{M_t}{M_\infty} = \left( \frac{1+\alpha}{\alpha} \right) \frac{6}{3} \left( \frac{D}{\pi} \right)^{1/2} \sqrt{t}$$

ANALYTICAL METHOD FOR PARTICLES (Cont.)

All equations to this point assume the initial concentration of gas in the fluid to be zero.

If the concentration of gas in the fluid is not initially zero but is at some pressure  $P_s$ , then the following applies (16,3):

The concentration of gas in the solid is  $S_P$ s in equilibrium with  $C_s$  (Concentration of gas in fluid before experiment starts) in the fluid. If at time  $t = 0$ ,  $C_s$  becomes  $C_0$  and  $C_0 < C_s$  then the amount of gas desorbed from the solid from  $t = 0$  is  $(M_t)$ .  $M_\infty$  is amount of gas desorbed from the solid in infinite time and  $M_s$  is the gas adsorbed by the solid up to time zero.

According to Schettler, then  $M_t - M_s =$  effective amount of gas desorbed from the solid after time  $t$ .  $M_\infty - M_s =$  effective amount of gas desorbed from the solid after infinite time (16).

Equation 4 becomes

$$5 \quad \frac{M_t - M_s}{M_\infty - M_s} = \left( \frac{1 + \alpha}{\alpha} \right) \frac{6}{\pi} \left( \frac{D}{t} \right)^{1/2} \sqrt{t}$$

It is necessary to get  $\frac{M_t - M_s}{M_\infty - M_s}$  and  $\alpha$  in terms of pressures measured by the apparatus. It has been shown that (3);

$$6 \quad \frac{M_t - M_s}{M_\infty - M_s} = \frac{P_t - P_0}{P_\infty - P_0} \quad \text{and} \quad \alpha = \frac{P_\infty - P_s}{P_0 - P_\infty}$$

$P_s$  = initial equilibrium pressure before zero time

$P_0$  = pressure at zero time

$P_\infty$  = pressure at infinite time

$P_t$  = measured pressure

All pressures have units of torr.

By substituting equations 6 and 5, equation 5 becomes

$$7 \quad \frac{P_t - P_0}{P_\infty - P_0} = \frac{P_0 - P_s}{P_\infty - P_s} \frac{6}{\pi} \left( \frac{D}{t} \right)^{1/2} \sqrt{t}$$

$P_\infty$  is determined after equilibrium is reestablished and usually takes about 15 minutes. Rewriting equation 7 for  $P_t$  gives

$$8 \quad P_t = P_0 + \left( \frac{P_0 - P_s}{P_\infty - P_s} \right) \left( \frac{P_\infty - P_0}{\sqrt{\pi}} \right) \frac{6\sqrt{D}}{\pi} \sqrt{t}$$

### ANALYTICAL METHOD FOR PARTICLES (Cont.)

A plot of  $Pt$  and  $\sqrt{t}$  gives a slope ( $E_1$ ) where

$$\underline{2} \quad E_1 = \left( \frac{P_c - P_s}{P_\infty - P_s} \right) \left( \frac{P_0 - P_c}{\sqrt{\pi}} \right) \frac{6\sqrt{D}}{3}$$

Given the slope ( $E_1$ ),  $D$  can be calculated.

The value of  $D$  can then be put into the general equation for desorption from particles; equation 6.30 (Crank, 7, p. 94).

In all cases tested, this experimentally determined  $D$  was found to be the solution for the general equation (equation 1).

### ANALYTICAL METHOD FOR SLABS

The problem can be stated mathematically in terms of solute diffusing into a fluid (7, pp. 56-60). Initial conditions are that the concentration of solute in the solid is  $SP_s$  and the concentration in the fluid is zero.

A general solution of the diffusion equation in a form expressing the total amount of solute leaving the sheet up to time  $t$  ( $Mt$ ) as a fraction of the corresponding quantity after infinite time ( $M^\infty$ ) is

$$\underline{1} \quad \frac{Mt}{M^\infty} = 1 - \sum_{n=1}^{\infty} \frac{2\alpha(1+\alpha)}{1+\alpha+\alpha^2 q_n^2} \exp\left(-\frac{Dq_n^2 t}{L^2}\right)$$

where  $q_n$ s are non-zero positive roots of  $\tan q_n = -\alpha q_n$  and  $\alpha = \frac{a}{SL}$  where  $S$  is the solubility factor of gas in the shale and  $L$  is half the slab thickness and  $a$  is the dimension of the fluid space on one side of the slab.

The smaller the value of  $Dt/L^2$  is, the more terms in the series of equation 1 are needed for a given accuracy. An alternative form of solution for small times is

$$\underline{2} \quad \frac{Mt}{M^\infty} = (1 + \alpha) \left\{ 1 - \exp\left(\frac{\tau}{\alpha^2}\right) \operatorname{erfc}\left(\frac{\tau}{\alpha^2}\right)^{1/2} \right\}$$

$$\text{where } \tau = \frac{Dt}{L^2}$$

The functions are defined as, (3, p. 113).

$$\underline{3} \quad \exp x^2 \operatorname{erfc} x \equiv e \operatorname{erfc} x \quad \text{and}$$

$$e \operatorname{erfc} x = 1 - \frac{2x}{\sqrt{\pi}} + x^2 - \frac{2x^3}{3\sqrt{\pi}} + \frac{x^4}{4} + \dots$$

ANALYTICAL METHOD FOR SLABS (Cont.)

Equation 2 then becomes

$$\underline{4} \quad \frac{M_t}{M_\infty} = \left( \frac{1+\alpha}{\alpha} \right) \frac{z}{\sqrt{\pi}} \frac{(Dt)^{1/2}}{L}$$

However, the experimental procedure involves desorption into a gas that does not have zero concentration initially (16). Thus, the gas adsorbed into the slab up to time zero must be taken into account.

First, define  $M_s$  as the amount of gas adsorbed on the rock before time zero. Then equation 4 becomes

$$\underline{5} \quad \frac{M_t - M_s}{M_\infty - M_s} = \left( \frac{1+\alpha}{\alpha} \right) \frac{z}{\sqrt{\pi}} \frac{(Dt)^{1/2}}{L}$$

As for particles, it is convenient to have  $\frac{M_t - M_s}{M_\infty - M_s}$  and  $\alpha$  in terms of pressures that are measured within the apparatus. Then equation 5 becomes

$$\underline{6} \quad \frac{P_t - P_0}{P_\infty - P_0} = \frac{P_0 - P_s}{P_\infty - P_s} \frac{z}{\sqrt{\pi}} \frac{(Dt)^{1/2}}{L}$$

$P_\infty$  for slabs cannot be determined conveniently as the time involved is measured in days or weeks in contrast to particles.

To eliminate  $P_\infty$  in the expression, the following substitution is made.  $\alpha$  can be defined as:

$$\underline{7} \quad \alpha = \frac{N_B}{SV_s} = \frac{P_\infty - P_s}{P_0 - P_\infty}$$

where  $N_B$  is defined as moles of gas in the gas phase per torr of pressure.

$$V_s = AL = \text{volume of solid (cm}^3\text{)}$$

$$S = \text{gas solubility in the solid}$$

Rewriting equation 6 for  $P_t$  and substituting equation 7 into equation 6 gives

$$\underline{8} \quad P_t = P_0 + (P_s - P_0) \frac{AS}{N_B} \frac{z \sqrt{D}}{\sqrt{\pi}} \sqrt{t}$$

Expression 8 shows no dependence on slab thickness for short times.  $N_B$  is calculated from the respective volumes and temperatures of each part of the cell. The solubility of the gas in the shale is determined from separate measurement of particle isotherms. The value of the slope of equation 8 then determines  $D$ , the diffusion coefficient for the slab.

### DEVELOPMENT OF SPECIFIC DEGASIBILITY

A relationship has been developed by Dr. Paul Schettler between the amount of gas released for a given surface area, duration, gas concentrations, and diffusivity (15,18). This concept was developed because of the inverse relationship between gas solubility and diffusivity exhibited by actual rock samples. Schettler developed a single combined parameter that would describe the potential productivity of rocks.

The basic relationship is given by Crank (7, p.32) and it is an empirical relation for the rate of production. The production rate is

$$\underline{1} \quad \frac{dMt}{dt} = (C_2 - C_0) A \left(\frac{D}{\pi t}\right)^{\frac{1}{2}}$$

The total amount of gas that desorbed from the rock in time  $t$  is  $Mt$

$$\underline{2} \quad Mt = 2 (C_2 - C_0) A \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$

$P_0$  is the well head pressure kept constant, with the concentration of gas in the rock,  $C_0$ , in equilibrium with the gas at pressure  $P_0$ .  $C_2$  is the initial concentration of gas in the rock before degassing.

The relation between concentration  $C$ , and pressure  $P$ , is given by  $C = SP$  where  $S$  is the gas solubility in the rock.  $S$  has been found to be linear (17). Rewriting equation 2

$$\underline{3} \quad Mt = 2 (P_2 - P_0) AS \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}}$$

The specific degasibility  $G$ , is defined as

$$\underline{4} \quad G = S \left(\frac{D}{\pi}\right)^{\frac{1}{2}}$$

Combining equations 3 and 4 gives

$$\underline{5} \quad Mt = 2 (P_2 - P_0) G A t^{\frac{1}{2}}$$

$G$  is also closely related to laboratory studies of degassing upon a known pressure decrease within the apparatus.

Specific degasibility can be written in the same form for particles and slabs. The expression for particles is

$$\underline{6} \quad Pt = P_0 + (P_2 - P_0) \frac{6 G (t)^{\frac{1}{2}}}{a S'} \left(\frac{P_0 - P_\infty}{P_\infty - P_s}\right)$$

The amount of gas desorbed in the process at STP is,

$V_{STP} = v S' (P_\infty - P_s)$  where  $v$  = volume of particles and  $S'$  is the volume of gas per volume of rock per torr pressure.

### DÉVELOPMENT OF SPECIFIC DEGASIBILITY (Cont.)

The gas given to the system at STP is,

$V_{STP} = N_B (P_\infty - P_0) RT$  where  $N_B$  is moles of gas in the gas phase per torr pressure.

The change in the amount of gas desorbed from the shale plus the change in amount of gas entering the system must equal zero.

$$vS' (P_\infty - P_s) = - N_B (P_\infty - P_0) RT$$

Solving for  $S'$  gives

$$S' = \frac{N_B (P_0 - P_\infty) RT}{(P_\infty - P_s)}$$

Substituting the above into equation 6 gives

$$\underline{7} \quad P_t = P_0 + \frac{P_s - P_0}{N_B RT} \frac{6v}{a} G (t)^{\frac{1}{2}}$$

$v = N \frac{4}{3} \pi a^3$  and area =  $N 4 \pi a^2$  where  $N$  is the number of spheres. The ratio of area to volumes gives  $\frac{A}{v} = \frac{3}{a}$ .

$G$  in terms of the slope of equation 7 becomes

$$\underline{8} \quad G = \frac{E_1 N_B RT}{2A(P_s - P_0)}$$

$G$  has units of cc gas per cm<sup>2</sup> rock · torr · (t)<sup>1/2</sup>

The expression for slabs is

$$\underline{9} \quad P_t = P_0 + 2 (P_s - P_0) \frac{GA}{N_B} (t)^{\frac{1}{2}}$$

To convert  $G$  from moles of gas to volume of gas in the gas phase,  $V = N_B RT$  for isothermal conditions at STP.

$$\text{Equation 9 becomes } P_t = P_0 + 2 (P_s - P_0) \frac{GA}{N_B RT} (t)^{\frac{1}{2}}$$

$G$  in terms of the slope of equation 9 becomes

$$\underline{10} \quad G = \frac{E_1 N_B RT}{2A(P_s - P_0)}$$

Thus  $G$  has the same units for both particles and slabs and is calculated by the computer in essentially the same manner.

### COMPARISON OF DATA

Initially all data were converted to comparable units of darcys or cm<sup>2</sup>/sec. A formula was developed at METC by James Mercer (Computer/Math Branch) and the author. It was derived from the basic definitions of

COMPARISON OF DATA (Cont.)

permeability (units of darcys) and diffusivity (units of  $\text{cm}^2/\text{sec.}$ ). The formula is

$$K = \frac{\mu R T S}{(0.987 \times 10^{-8}) P} D$$

where permeability (K) is in darcys and diffusivity (D) in  $\text{cm}^2/\text{sec.}$   
 $\mu$  is viscosity of the permeating gas in poises ( $\frac{\text{dyne} \cdot \text{sec.}}{\text{cm}^2}$ ) and is temperature dependent.

R is the gas constant  $82.056 \frac{\text{cc} \cdot \text{atm}}{\text{mole} \cdot \text{K}}$

T is the average temperature in degrees Kelvin (K)

S is the gas solubility in the shale, given as  $1.11 \times 10^{-5}$  moles gas/cc rock/atm (16).

P is the average pressure against the slab face from which gas permeated. If P is given in atmospheres, it must be converted to  $\text{dyne}/\text{cm}^2$  since  $\mu$  is in poises.

Table 1 gives the averaged permeation values for each laboratory. There is a remarkable similarity in the average results considering the different method that were used.

Battelle had many samples for which no permeation was detected (zero values) (7). These were samples that showed no permeation after 15 minutes, at which time, the experiments were discontinued. The table includes two sets of data for Battelle, those without the zero values and those with the zeros values. Alfred's results were consistently high but this was probably due to the presence of invisible natural fractures as stated in their report (2).

Tables II through VIII show the comparison of values determined by each laboratory both in darcys and  $\text{cm}^2/\text{sec}$  for each well. Table IX includes additional data that Battelle compiled for three wells.

For well 20338 (Wise Co., VA), Battelle's data was consistently lower than Juniata's. All Juniata's data was from particles.

For well 20403 (Lincoln Co., WV), Battelle showed no permeability. Juniata found diffusivity perpendicular to bedding generally lower than for well 20338. Juniata also had a small amount of data that showed diffusivity parallel to bedding was not necessarily greater than that perpendicular to bedding.

Three labs did experimental work on well 20336 (Martin Co., KY). Alfred's data was much greater than Juniata's. All Juniata's data was from particles. Battelle again found no permeability.

The permeabilities found by Battelle were unexpectedly low considering their use of helium gas. Grahams Law (10) relates the molecular weight of a gas to the diffusion flux. The helium molecules should diffuse twice as fast as methane molecules under the same gas concentration. However, the data does not support this.

## COMPARISON OF DATA (Cont.)

In order to elucidate the diffusion coefficient, Tables III, V, VII, VIII, and IX, give the mean square displacement ( $\bar{x}^2 = 2Dt$ ) of methane molecules for one inch, one foot, 10 years and 30 years. If there were more than one value for diffusivity (D) for a particular depth, the calculations were based on the smallest value.

The average diffusivity in  $\text{cm}^2/\text{sec}$  for gas diffusing perpendicular to bedding for Juniata was  $1.9 \times 10^{-7}$ , for Battelle  $0.008 \times 10^{-7}$  and for METC,  $0.79 \times 10^{-7}$ . These correspond to a travel distance one foot in 77 years, 18,400 years and 186 years, respectively. In 30 years, the corresponding distances traveled would be 7.5, 0.5 and 4.8 inches, respectively.

## CONCLUSIONS

Battelle Labs used a flow through method based on Darcy's law. Problems with this procedure occur when this law becomes invalid. For gases, this occurs at very low velocities and when the pore diameter becomes comparable or less than the molecular mean free path of the flowing gas (14, pp. 75,71). The pore structure is not known for the shales, and the flow velocities may be too low for these calculations. Thus the Battelle data is lacking in precision to some degree.

Alfred University used a flow through method based on Darcy's law with backpressure buildup on the manometer taken into account. It was an approximate steady state analysis applied to a non-steady state process. The results should be considered an approximation.

The METC procedure was a flow through method using methane. An exact analytical solution was used. The solubility of gas in the shale was not known but an average value was used in the calculations.

Juniata College is using a desorption method to determine diffusion coefficients and degasibility for slabs and particles. It is an exact mathematical analysis. Solubility and diffusivity are determined for the particles. However, for slabs, the solubility is determined from particle data found for the same depth, and that determines the slab diffusivity. Specific degasibility for both particles and slabs is determined. A separate solubility measurement is not required.

Mound Labs is using a flow through method based on Darcy's law with corrections for gas flow. A sufficiently large (6, p. 50) mean pressure yields the best results. If diffusion is occurring, this procedure will be inaccurate. However, it may be difficult to determine when diffusion mechanisms are taking place.

All the data were converted to darcys and to  $\text{cm}^2/\text{sec}$  (see Part II, Comparison of Data). The data for wells 20336 and 20338 show that the conversion to darcys make the values between laboratories appear closer than if they were converted to  $\text{cm}^2/\text{sec}$ . This is due largely to the conversion factor between darcys and  $\text{cm}^2$  (1 darcy =  $0.987 \times 10^{-8} \text{ cm}^2$ ). This factor has the effect of increasing values in the conversions from

CONCLUSIONS (Cont.)

D to K and decreasing values in the conversions from K to D. In addition, because the pressure was low in both Juniata's and Battelle's experiments, the pressure term adds to the effect of the conversions.

There may not be enough data to make good comparisons, especially for slabs. However, the following general statements can be made. Alfred's high values probably reflects the existence of microfractures in the samples. Battelle's values were small in comparison to Juniata's desorption data. This was possibly due to such a low gas flow that Battelle's method of calculation was no longer valid. Most of the values found at METC were smaller than Juniata's. This indicates that the diffusion flux was much larger for Juniata but because different wells were involved, direct comparisons cannot be made.

Desorption experiments and flow through experiments would be expected to give nearly the same results with the same shale samples if exact analytical solutions were used. After a comparison of data between Juniata and METC for slabs with diffusion perpendicular bedding (Tables III and VIII), it was found that this was generally the case.

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APPENDIX A

Table I AVERAGE DIFFUSION VALUES

Permeability (Darcys x 10 <sup>-8</sup> )		Diffusivity (cm <sup>2</sup> /sec x 10 <sup>-7</sup> )	
Orthogonal to Bedding	Overall Parallel to Bedding Average	Orthogonal to Bedding	Overall Parallel to Bedding Average
Battelle Labs			
0.04	0.78	0.001	0.004
0.29	1.96	0.007	0.02
		Includes Zeros	
		Excludes Zeros	
Alfred University			
6.93	222	141	1295
Juniata College			
0.10	2.57	1.94	7.4
		19.9	
METC - DOE			
0.02	0.02	0.79	0.79

Table II WELL # 20403, Lincoln Co. WV Permeabilities (Darcys x 10<sup>-9</sup>)

Depth (feet)	Battelle		Juniata		Juniata Particles-Methane
	Slabs-Helium Orthogonal to Bedding	Slabs-Helium Orthogonal to Bedding	Slabs-Methane Parallel to Bedding	Slabs-Methane Parallel to Bedding	
2,736			0.637		0.142
2,746	0				
2,806					0.880
2,836					0.702
2,852	0				
2,936					1.75
3,036					3.09
3,064	0				
3,096					1.70
3,156					1.19
3,165	0				
3,221					2.16
3,231					0.53
3,268	0				
3,281					1.64
3,366	0				
3,386					0.37
3,396					5.45
3,406					0.26
3,426			0.070	0.030	
3,446			0.082		
3,593	0				
3,596					2.01
3,686				9.23	1.39
3,736					1.12
3,766					1.76
3,797	0				
3,986			0.132	0.381	

Table III WELL # 20403, Lincoln Co. WV Diffusivities ( $\text{cm}^2/\text{sec} \times 10^{-4}$ )

Depth (feet)	Battelle Slabs-Helium		Juniata Slabs-Methane		Juniata Particles-Methane	Time to Move		Distance Moved in	
	Orthogonal to Bedding	Parallel to Bedding	Orthogonal to Bedding	Parallel to Bedding		One Inch (days)	One Foot (years)	10 years (feet)	30 years (feet)
2,736		12.5			3.98	94	37	0.5	0.9
2,746	0								
2,806					2.80	133	53	0.4	0.8
2,836					6.31	59	23	0.7	1.1
2,852	0								
2,936					16.0	23	9	1.0	1.8
3,036					26.5	14	6	1.3	2.3
3,064	0								
3,096					14.08	27	11	1.0	1.7
3,156					9.87	38	15	0.8	1.4
3,165	0								
3,221					19.2	20	8	1.1	2.0
3,231					4.8	78	31	0.6	1.0
3,268	0								
3,281					14.2	27	10	1.0	1.7
3,366	0								
3,386					3.02	124	49	0.5	0.8
3,396					5.06	74	29	0.6	1.0
3,406					2.2	169	67	0.4	0.7
3,426						634	250	0.2	0.3
3,446					1.652	269	106	0.3	0.5
3,593	0				1.395				
3,596									
3,686				220.0	18.6	20	8	1.1	1.9
3,736					11.57	20	13	0.9	1.5
3,766					9.86	38	15	0.8	1.4
3,797	0				15.4	24	10	1.0	1.8
3,986					2.775	135	53	0.4	0.8

Table IV WELL # 20338, Wise Co. WV Permeabilities (Darcys x 10<sup>-8</sup>)

Depth (feet)	Battelle		Juniata Particles-Methane
	Slabs-Helium Orthogonal to Bedding	Slabs-Helium Parallel to Bedding	
4,871			0.55
4,872	0		
4,882	0		
4,912	0		7.22
4,921			
4,922		.112	
4,950		0	
4,960		0	
4,970		0	
4,971			2.28
5,211			2.49
5,232	0		
5,261			7.49
5,283	0		
5,293	0		
5,303	0		8.32
5,311			
5,312		.067	
5,322	0		
5,332		0	
5,347	0		
5,357	0		
5,361			2.96
5,362	0		
5,372	0		
5,404	0		
5,414	.056		
5,424	0		
5,434	0		
5,444	0		
5,447	.067		
5,461			2.28
5,467	.0091		

Table V WELL # 20338, Wise Co., VA Diffusivities ( $\text{cm}^2/\text{sec} \times 10^{-7}$ )

Depth (feet)	Battelle		Junlata Particles-Methane	Time to Move		Distance Moved in	
	Slabs-Helium Orthogonal to Bedding	Parallel to Bedding		One Inch (days)	One Foot (years)	10 years (feet)	30 years (feet)
4,871			5.25	71	28	0.6	1.0
4,872	0	0					
4,882							
4,912	0		61.4	6	2	2.0	3.5
4,921				365	52,570	0.01	0.02
4,922		.0028					
4,950		0					
4,960		0					
4,970		0	16.6	23	9	1.1	1.8
4,971							
5,211			16.7	22	9	1.1	1.8
5,232	0						
5,261	0		49.7	8	3	1.8	3.2
5,283	0						
5,293	0						
5,303	0						
5,311			74.8	5	2	2.3	3.9
5,312		.0017		601	86,590	0.01	0.02
5,322	0						
5,332	0	0					
5,347	0						
5,357	0						
5,361	0		22.5	17	7	1.2	2.1
5,362	0						
5,372	0						
5,404	0						
5,414	.0014			730	105,140	0.01	0.02
5,424	0						
5,434	0						
5,444	0						
5,447	.0017			601	86,590	0.01	0.02
5,461			20.9	18	7	1.2	2.1
5,467	.00023			4,444	639,980	0.004	0.007

Table VI Well #20336, Martin Co., KY Permeabilities (Darcys x 10<sup>-8</sup>)

Depth (feet)	Alfred		Battelle		Juniata Particles-Methane
	Orthogonal to Bedding	Slabs-Air Parallel to Bedding	Orthogonal to Bedding	Slabs-Helium	
2,479					1.46
2,493.5	3.76	62.7			
2,499.8		16.0			
2,506.2		35.0			
2,541.8	10.1	260.0			
2,555.6		175.0			
2,570.1		1003.0			
2,572.1		2.0			
2,579			0		2.33
2,595					
2,629					
2,681					2.14
2,730					6.02
2,745			0		1.94
2,781					7.50
2,833					6.72
2,881					2.11
2,911			0		
2,931			0		0.43
2,999					
3,019			0		
3,031					0.84
3,131					
3,137			0		1.82
3,138			0		
3,231			0		
3,244					1.70
3,281					2.63
3,331					
3,381					1.86
3,394					8.55

Table VII Well # 20336, Martin, Co., KY Diffusivities (cm<sup>2</sup>/sec x 10<sup>-4</sup>)

Depth (feet)	Alfred		Battelle		Juniata Particles-Methane	Time to Move		Distance Moved in	
	Orthogonal to Bedding	Parallel to Bedding	Släbs-Helium Orthogonal to Bedding	Orthogonal to Bedding		One Inch (days)	One Foot (years)	10 years (feet)	30 years (feet)
2,479					12.0	31	12	0.9	1.6
2,493.5	76.6	128.0				3	1	2.9	5.2
2,499.8		326.0				1	0.5	4.6	8.2
2,506.2		713.0				0.5	0.2	6.9	12.1
2,541.8	205.8	5300				1.7 hrs	10.1 days	19.0	32.8
2,555.6		3570				12.5 hrs	15.1 days	15.4	26.9
2,570.1		20,400				0.4 hrs	2.6 days	37.1	64.6
2,572.1		40.8				9	4	1.7	2.9
2,579					19.73	19	8	1.2	2.0
2,595			0						
2,629					19.08	20	8	1.1	2.0
2,681					52.9	7	3	1.9	3.3
2,730					14.9	25	10	1.0	1.7
2,745			0						
2,781					15.7	24	9	1.0	1.8
2,833					61.3	6	2	2.0	3.5
2,881					17.89	21	8	1.1	1.9
2,911									
2,931					3.25	115	45	0.5	0.8
2,999			0						
3,019									
3,031					7.47	50	20	0.7	1.2
3,131									
3,137					11.9	31	12	0.9	1.6
3,138			0						
3,231					15.5	24	10	1.0	1.8
3,244			0						
3,281					17.5	21	8	1.1	1.9
3,331					16.2	23	9	1.0	1.8
3,381					60.1	6	2	2.0	3.5
3,394			0						

TABLE VIII

Well Number and Depth (feet)	Permeability (Darcys x 10 <sup>-8</sup> )		Diffusivity (cm <sup>2</sup> /sec x 10 <sup>-7</sup> )		Time to Move One Inch (years)	Distance Moved in 10 years (feet)	Distance Moved in 30 years (feet)
	Battelle Slabs-Helium Orthogonal to Bedding	MERC Slabs-Methane Orthogonal to Bedding	Battelle Slabs-Helium Orthogonal to Bedding	MERC Slabs-Methane Orthogonal to Bedding			
#109 Washington Co. OH							
3495	0	.00032	0	.0106	96	13,890	0.05
3544							
3545	0		0				
3605	0		0				
3644	0		0				
3711	0		0				
#11940 Jackson Co. WV							
3481.5		.00032		.011	93	13,380	0.05
3636.4		0.134		4.7	0.26	38	0.9
3778.9		0		0			
3779.0		.00034		.011	93	13,380	0.05
3787.9		.00062		.020	51	7360	0.06

TABLE IX

Well Number and Depth (feet)	Permeability (Darcys X 10 <sup>-8</sup> ) Battelle Slabs-Helium		Diffusivity (cm <sup>2</sup> /sec X 10 <sup>-7</sup> ) Battelle Slabs-Helium		Time to Move One Inch   One Foot (years)		Distance Moved In 10 years   30 years (feet)	
	Orthogonal to Bedding	Parallel to Bedding	Orthogonal to Bedding	Parallel to Bedding	One Inch	One Foot	10 years	30 years
#RAR-1 Henderson Co., IL 321 411	0.203 0		0.00515 0		198	28,580	0.02	0.03
#RC-1 Christian Co., KY 2183 2191 2220 2230 2339 2251 2259 2271 2281 2290 2300	0 0.53 0 0.079 0 0 0 0 0 0	0.56 0	0 0.0135 0 0.00201 0 0 0 0 0 0	0.0142 0	76 72 509 6	10,900 10,370 73,230 820	0.03 0.03 0.01 0.11	0.05 0.05 0.02 0.19
#1-D Effingham Co., IL 3012 3043 3051 3056 3063 3067 3074 3080 3086 3094 3099 3100	0 0 0 0.018 1.4 0 0 0 0.11 0.46 0 0		0 0 0 0.000457 0.0355 0 0 0 0.00279 0.0117 0 0		2240 29 366 87	322,090 4,150 52,760 12,580	0.006 0.05 0.01 0.03	0.01 0.08 0.02 0.05

## APPENDIX B

AREA CALCULATIONS OF FRACTURE SYSTEMS

Knowledge of the diffusivity (D) and solubility (S) of gas in the shale allows calculations of certain unknown parameters of the gas-shale system.

One of the few wells for which all pertinent physio-chemical parameters are known is well #11940 (Jackson Co., WV). This gas well has not been stimulated and yet has produced high volumes since it started to flow in October 1975.

The original formation pressure was 190 psig and the line pressure was 85 psig. D was found to be  $1.1 \times 10^{-9}$  cm<sup>2</sup>/sec and S to be 0.252 cc gas/cc rock/atmosphere. The production zone was around the depth of 3750 feet.

The integration of the rate equation (Schettler, 13) gives the empirical equation relating production and time.

$$Mt = 2A (P_2 - P_0) S \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} = 2 (P_2 - P_0) G A (t)^{\frac{1}{2}}$$

All the parameters in the above equations are constant except time and the production.

When the production is calculated from a given rate, care must be exercised in choosing the time interval for calculating the area. This is because the effect of the equation is to give different areas depending on the time interval chosen. In order to accurately determine the area, the production must be known for a particular time interval.

Gas production with time eventually levels out and this flat production is due only to gas diffusion into the fracture system connected to the well bore (13). The available data was fitted to an exponential decline curve (Appendix C) and the asymptote was found to be about 23,000 cu ft/day.

The production equation given above allows the calculation of the area required to give that particular production for one day. The natural fracture area for well #11940 was calculated to be  $3.562 \times 10^7$  square feet. One way to visualize this area is to assume a circular fracture with the well bore at the center. The radius of such a circular fracture would be 2380 feet.

## APPENDIX C

FLAT PRODUCTION RATE PREDICTION

Many of the shale gas wells eventually settle into a constant production rate after a number of years. These wells must have essentially an infinite source of gas available to their fracture network.

Often only the first few years of production data are available for a particular well. An estimate can be made of the flat part of the curve that would occur after 25 or 30 years by fitting the data to some kind of decline curve. This decline can be considered either hyperbolic or exponential. Using the peak production year as the first year and the following year as the second year, results in two equations in two unknowns. The solution is for  $b$ , the theoretical constant production as time becomes large.

For the hyperbola, the equation is,

$$y = \frac{a^2}{2x} + b; x \geq 0$$

$y$  is the production rate per year, usually in MMCF

$x$  is the time interval in years

$a$  is the absolute value of the foci

$b$  is the asymptote

For the exponential decline curve, the equation is,

$$y = \frac{i - b}{e^{0.25x}} + b; x \geq 0$$

The coefficient of the independent variable was selected from an average value as 0.25.  $x$  and  $y$  are the same as above and  $i$  is the  $y$  intercept (the theoretical initial production at time zero).  $b$  is the asymptote.

Both equations were tested on production data. The hyperbolic fit gave good results for a few wells, but in general, the exponential fit gave the best prediction of  $b$ . For a few wells, the exponential gave a negative  $b$ . In those cases, the hyperbolic equation found a reasonably accurate  $b$ .

Therefore, when using the above procedure, all calculations should first be made on the basis of the exponential fit. But if  $b$  is a negative number, then the hyperbolic fit should be used for the prediction.