ESTIMATION OF ADSORPTION PARAMETERS FROM EXPERIMENTAL DATA

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THE DEPARTMENT OF PETROLEUM ENGINEERING
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By
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I certify that I have read this report and that in my opinion it is fully adequate, in scope and in quality, as partial fulfillment of the degree of Master of Science in Petroleum Engineering.

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Abstract

In this study, pressure transient tests in a steam filled core were carried out. Eight different rock samples were tested and the adsorption isotherm parameters were estimated by using nonlinear regression. Good matches to the pressure transient curves were obtained and from them the adsorption isotherm parameters were inferred. Preliminary results show that the nonlinear regression method can be applied to adsorption related geothermal reservoir studies. It was also, found that differences in reservoir permeability and porosity did not affect the characteristic shape of the isotherm curves derived by using this estimation procedure.

Chapter 1

Introduction

When a gas or vapor is brought in contact with an evacuated solid, a part of it may be taken up by the solid. If this occurs at constant volume, the pressure drops; if at constant pressure, the volume decreases. The molecules that disappear from the gas phase either enter the inside of the solid, or remain on the outside, attached to its surface. The former phenomenon is called absorption; the latter adsorption. The solid that takes up the gas or vapor is called the adsorbent, the gas or vapor attached to the surface of the solid is called the adsorbate. Often the two occur simultaneously, the total uptake of the gas is then designated by the term sorption.

There are two types of adsorption exist: physical,adsorption (physisorption) and chemical adsorption (chemisorption). Physisorption involves intermolecular forces (van de Waals forces, hydrogen bonds, etc.) whereas chemisorption is connected with the formation of a chemical compound involving the adsorbent and the primary layer of the substance adsorbed. Steam adsorption on the solid is considered as physical adsorption.

The phenomenon of adsorption has long been known. As early as in 1777 Fontana (1777) had noted that freshly calcined charcoal, cooled under mercury, was able to take up several times its own volume of various gases; and in the same year Scheele (1777) recorded that air expelled from charcoal on heating was taken up again on cooling. It was soon realized that the volume taken up varies from one charcoal to another and from one gas to another. In suggesting that the efficiency of the solid depended on the area of exposed surface, de Saussure (1814) anticipated our present-day views on the subject. Mitscherlich (1843), on the other hand, emphasized the role of the pores in charcoal, and estimated their average diameter to be 1/2400 in; it would seem that carbon dioxide condensed into layers 0.005 mm thick in a form closely resembling liquid carbon dioxide. These two factors, surface area and porosity (or pore volume), are now recognized to play complementary parts in adsorption phenomena, not only in charcoal but in a vast range of other solids. It thus comes about that measurements of adsorption of gases or vapors can be made to yield information as to the surface area and the pore structure of the solid.

The pore systems of solids are of many different kinds. The individual pores may vary greatly both in size and in shape within a given solid, and between one solid and another. A feature of special interest for many purposes is the "width w" of the pores, e.g. the diameter of a cylindrical pore, or the distance between the sides of a slit-shaped pore. According to the International Union of Pure and Applied Chemistry (IUPAC) (1972), pores are divided into three classes: micropores, mesopores and macropores. The classification of the three category is summarized in Table 1.

Table 1. Classification of pores according to IUPAC(1972)

	Width w
Micropores	Less than 20 Å
Mesopores	Between 20 Åand 500 Å
Macropores	More than 500 Å

The basis of the classification is that each of the size ranges corresponds to characteristic adsorption effects as manifested in the isotherm. In micropores, the interaction potential is significantly higher than in wider pores owing to the proximity of the walls, and the amount adsorbed (at a given relative pressure) is correspondingly enhanced. In mesopores, capillary condensation, with its characteristic hysteresis loop, takes place. In macropores, the pores are so wide that it is virtually impossible to map out the isotherm in detail because the relative pressures are so close to unity.

For a given gas or vapor and unit weight of a given adsorbent the amount of gas or vapor adsorbed at equilibrium is a function of the final pressure and temperature only,

$$a = f(p, T) \tag{1.1}$$

where a is the amount adsorbed per gram of adsorbent, p in the equilibrium pressure, and T is the absolute temperature. Usually either the pressure or the temperature alone is varied, while the other is kept constant. When the pressure of the gas or vapor is varied and the temperature is kept constant, the plot of the amount adsorbed against the pressure is called the adsorption isotherm, and the isotherm equation is:

$$a = f(p) \quad T = constant \tag{1.2}$$

When the temperature is varied and the pressure is kept constant, one obtains the adsorption isobar:

$$a = f(T) \quad p = constant \tag{1.3}$$

The adsorption isotherm is the most widely used in the field of adsorption. In studying the adsorption/desorption phenomenon associated with vapor-dominated geothermal reservoirs, we use the adsorption/desorption isotherm with the unit of gram of water adsorbed per gram of solid (gram water adsorbed)/(gram solid).

Vapor-dominated geothermal reservoirs occur when the fluid pressure in the producing zone is at or below the saturation pressure corresponding to the reservoir temperature. Only a few geothermal fields in the world satisfy this criterion. These include the Geysers field in northern California and the Larderello field in Italy. Although they are few in number, the vapor-dominated geothermal reservoirs offer the most readily used form of geothermal fluid, namely high enthalpy, used to power turbines for the generation of electricity.

Studies of reservoir and production behavior of vapor-dominated geothermal system have focused on estimates of resource size, reservoir longevity and resource management. Traditionally, it has been considered that superheated steam and rock are the only two components in a dry steam geothermal reservoir like the Geysers. From the fundamental physical properties of fluid and rock, however, there should exist a certain amount of liquid in addition of steam. However the reservoir pressure at the Geysers is too low for water to exist in the form of bulk liquid at the reservoir temperature. It has been proposed that water might exist as adsorbed liquid in micropores (White, 1973; Hsieh, 1980). Evidence from both laboratory' studies and field data indicates that storage of liquid as micropore fluid is likely (Hsieh, 1980; Hsieh and Rarney, 1983; Nghiem and Ramey, 1990).

Based on different theories and assumptions, various explicit equations have been suggested for gas and vapor adsorption isotherm. The most often used two equations are the Langmuir (1916) isotherm and the Brunauer, Emmett, and Teller (BET) (1938) isotherm.

The Langmuir isotherm has the form:

$$X = \frac{P/P_{sat}}{A + BP/P_{sat}} \tag{1.4}$$

The BET isotherm has the form:

$$X = \frac{CP/P_{sat}}{(1 - P/P_{sat})[1 + (C-1)P/P_{sat}]} \tag{1.5}$$

Both the Langmuir equation and the BET equation were developed basing on similar assumptions. However, the Langmuir equation assumed a monolayer adsorption and the BET equation extended Langmuir's idea to multiple layer adsorption. Since in most realistic cases, adsorption is not monolayer, the Langmuir equation was thought not to be very useful. However, recent studies (1991) have shown that in some cases, the Langmuir equation appears to match experimental data over the entire range of pressure to the saturation pressure $(p/p_{sat} = 1)$ while the BET equation can only be used for a limited relative pressure range. This suggests that an equation of the form of Langmuir equation is probably a good empirical representation of adsorption data.

Recognizing the important effect adsorption might have on the estimation of geothermal reservoir performance, several models which considered the effects of adsorption have been developed and tested by different authors (Moench and Atkinson, 1978; Herkelrath, Moench and O'Neal, 1983). The most recent model was developed by Nghiem and Ramey (1990) and a simulator was developed to simulate the one-dimensional steam flow in a homogeneous porous media. Surprisingly, by fitting the experimental isotherm data, they found that the Langmuir isotherm could match several measured data over the entire relative pressure range to $P/P_{sat} = 1$ while the BET isotherm did not. By using the Langmuir isotherm, Nghiem and Ramey (1990) simulated one-dimensional flow in a geothermal reservoir and predicted the pressure change of the reservoir under specified production conditions.

To use the Langmuir isotherm (Eqn. 1.4), two coefficients have to be specified. Nghiem and Ramey determined them by fitting certain experimental data. However the adsorption isotherm is different from one system to another. For each system, a set of coefficients needs to be determined. Herkelrath et al. (1983) studied the transient flow of pure steam in a uniform porous medium and found that the time required for steam pressure transients to propagate through an unconsolidated material containing sand, silt, and clay was 10-25 times longer than predicted by conventional superheated steam flow theory. They concluded that the delay in the steam pressure breakthrough was caused by adsorption of steam in the porous sample. This originated the idea of estimating of adsorption parameters from pressure transient experiments.

In this study, a number of steam pressure transient experiments were carried out. Nghiem and Ramey's (1991) simulator was run in combination with a nonlinear regression program to simulate the precess. The steam pressure transient results are believed to reflect the affect of adsorption. By fitting the experimental pressure transient data, the Langmuir isotherm parameters can be extracted by using nonlinear regression.

Chapter 2

Previous Work

In 1980, Hsieh (1980) studied the vapor pressure lowering phenomenon in porous media and measured the adsorption/desorption isotherms of water vapor, methane, and ethane with several different core samples. The experiment proved that the water vapor pressure lowering in rock is dominated by micropore adsorption and Hsieh (1980) suggested that the adsorbed water may be an important source of steam in vapor dominated geothermal systems. Although Hsieh (1980) concluded that there were no significant hysteresis loops in water adsorption/desorption isotherm, some of his results did show visible differences between adsorption and desorption isotherms.

In 1983, Herkelrath, Moench, and O'Neal conducted laboratory investigations of steam flow in a porous medium. They ran the transient, superheated steam flow experiments by bringing a cylinder of porous material to a uniform initial pressure and then making a step increase in pressure at one end of the sample while monitoring the pressure transient breakthrough at the other end. They found the breakthrough time for steam pressure was 10-25 times longer than predicted by conventional (no adsorption) superheated steam flow theory. **A** new model including the effect of adsorption was developed and tested by using it to simulate the experimental pressure transient process. They assumed the steam pressure was a function of temperature and the amount of water adsorption:

$$P_v = P_v(T,S) = P_0(T)R(S) \tag{2.1}$$

where $P_0(T)$ represented the saturated vapor pressure function, and R(S) was the relative vapor pressure, which was a function of the fraction of the pore space that was filled with adsorbed water. To find out the function R(S), adsorption isotherm data were needed. So Herkelrath et al (1983) had to run additional tests similar to the those run by Hsieh and Ramey (1983) to measure the adsorption isotherm at equilibrium. Then by fitting the isotherm data with an empirical relation they obtained a function for R(S) of the following form:

$$R(S) = A(10^{-[10^{(B-S)C}]}) \tag{2.2}$$

where **A,** B, and C were constants determined by least squares fitting **(A=** 1.078, B=0.00821, C=0.0224 in their case). The results of the simulation were compared to the experimental data and good agreement between simulation and experimental results was achieved.

Economides and Miller (1985) also studied the effects of the adsorption phenomena in the evaluation of vapor-dominated geothermal reservoirs. In their study, the conventional models for material balance and pressure transient behavior were extended to incorporate the effects of adsorption. Again an adsorption isotherm was needed for calculation. They used a simple linear equation of the following form to calculate the isotherm approximately:

$$X = \sigma p/p^* \tag{2.3}$$

where X is the amount absorbed, σ is an experimental constant, p is the pressure and p^* is the saturated vapor pressure.

To do the calculation, 'the constant σ needs to be determined first. Economides and Miller (1985) used the constants obtained from the experiments by Hsieh (1980).

Nghiem and Ramey (1991) developed another model including adsorption to simulate a one-dimensional vapor dominated geothermal reservoir. The Langmuir isotherm (Eqn. 1.4) was used and the two constants in the equation **(A** and B) were determined from the experimental data from Herkelrath and O'Neal (1985), and from Herkelrath (1990). Then, performance forecasting for a hypothetical field with the

Geysers greywacke rock was performed to demonstrate the importance of the desorption. The results of Nghiem and Ramey also support the theory that adsorption is the dominant mechanism for steam storage in geothermal reservoir.

Michael Harr (1991) also measured the adsorption/desorption of steam in porous media in the laboratory. He ran a series of equilibrium measurements of the steam adsorption and desorption isotherms by using a sorptometer. Different geothermal field rocks were tested at different temperatures and the results were compared. Harr found that the adsorption and desorption isotherms measured at different temperature were different. Also there was a large hysteresis between adsorption and desorption. Harr also ran a pressure transient test using the equipment borrowed from USGS (the same equipment used by Herkrlrath et al in 1983). Four pressure transient curves were obtained. A large hysteresis between adsorption and desorption was observed.

All previous work strongly supports the theory that adsorption is the dominant reservoir storage mechanism in vapor-dominated geothermal reservoir and by including the effect of adsorption we can make better forecasts of the reservoir performance. One difficulty in doing this is that we require measured adsorption isotherm data. The measurement of adsorption isotherms in the laboratory requires specially designed equipment and is usually very time consumming. Another difficulty is that the steam adsorption isotherms are quite different from one rock to another. Therefore, the adsorption isotherm obtained from one rock sample can not be used for another. This restricts the usage of the simulators and thus makes their results less general.

Some of the previous works (Herklrath et al., 1983; Harr, 1991) also demonstrated that adsorption had a great effect on the pressure transient. By analyzing the pressure transient curves we might be able to infer the adsorption isotherm. This will eliminate the necessity of adsorption isotherm measurement and finally enable us to estimate the isotherm from field pressure decline curve. After all, the field pressure decline curve is usually available for most geothermal fields.

In this study, Michael Harr's vapor pressure transient experiment was continued, by using the same experiment equipment with some modification of the data acquisition system. More pressure transient data are made available. **A** computer program is developed combining the nonlinear regression and a one-dimensional simulator (Nghiem and Ramey, 1991). The method of estimating adsorption the isotherm from pressure transient curve is tested. Some of the estimated isotherm results are compared with the isotherm data obtained by Shang (1992) in equilibrium experiments.

Chapter 3

Experiment Apparatus and Procedures

3.1 Apparatus

The equipment used was built originally by Herkelrath et al. **(1983)** at the U.S.G.S. It is the same equipment that Michael Harr **(1991)** used in his experiment. Figure **3.1** shows a schematic diagram of the setup.

The equipment consists of four major parts: steam generator, air bath, vacuum system, and data recording system. The steam generator produces steam at a set temperature for the duration of the experiment. The air bath is used to maintain a constant temperature during **the** experiment, the vacuum system is used to outgas the sample before the transient run and evacuate the connecting tubes for pressure measurements. The data acquisition system used before in the transient test equipment was an old-fashioned Digital RXO2 computer with a VT105 monitor. The pressure transient data were first recorded on 8 inch floppy diskette. Then the diskette needed to be taken to the U.S.G.S. to have the data transferred from the diskette onto an IBM-PC or a Macintosh diskette for further use. This was very inconvenient. In this study, we successfully replaced the old monitor with an IBM-PC computer so that the pressure transient data can be seen and saved directly onto the IBM-PC. There is a detailed description and explanation about the structure and function of each part of the equipment in Appendix A of Michael Harr's report (Harr, 1991).

3.2 Samples Used in the Experiments by Michael Harr

In the previous transient experiments run by Michael Harr, four geothermal field rock samples were used. They are listed in Table 2.

Table 2: Rock Samples Used by Michael Harr

Location	Well	Size (mesh)	Sample Holder	
			Dia.(mm)	Length(mm)
Reykjanes(1000 m)	9	10 - 100	17.27	306.3
Geysers(5000'-5200')	Unknown	10 - 150	23.62	312.7
Geysers(5000'-5200')	Unknown	28 - 150	17.27	306.3
Geysers(5000'-5200')	OF52-11	10 - 150	23.62	312.7

The permeabilities were measured by flowing nitrogen through the samples. Klinkenberg effect was removed in all measurements.

3.3 Samples Used in the Present Experiment

In this study, eight rock samples were used. They are listed in the Table 3.

Table **3.** Rock Samples Used in Pressure Transient Experiment

Location	Well	Size (mesh)	Sample Holder	
			Dia.(mm)	Length(mm)
Geysers(5000'-5200')	Unknown	28 - 150	17.27	306.3
Geysers(5000'-5200')	OF52-11	10 - 150	17.27	306.3
Geysers(5000'-5200')	OF52-11	20 - 150	17.27	306.3
Montiverdi	2	10 - 150	17.27	306.3
Reykjanes(1000 m)	9	10 - 100	17.27	306.3
Geysers(8600'-8800')	Megu-15 ST2	20 - 150	17.27	306.3
Geysers(8000'-8200')	OF52-11	30 - 80	17.27	306.3
Geysers(8000'-8200')	OF52-11	30 - 150	17.27	306.3

3.4 Procedures

3.4.1 Experiment Procedures

First the system is set at a certain temperature and the whole system allowed to reach stability while continuously outgasing the sample for about twelve hours or more. Then pure steam of the same temperature is introduced into the sample to adsorb for about another twelve hours. After that, we can make measurements of the vacuum of the system, the initial steam pressure inside the sample holder (both at bottom and at the top), the saturated vapor pressure inside the air bath, and the atmospheric pressure at the time. Finally, we open the bottom of the sample holder to the atmosphere abruptly and let the pressure inside the sample holder decrease. The computer will record the pressure changing at the top of the sample holder with time. After the run, we measure the permeability of the sample and the sample's weight. Again there is a detailed description of the whole operation of the experiment part of the run in Michael Harr's report (Harr, 1991). In this study, we followed the operating procedures given in Harr's report.

3.4.2 Parameter Estimation Procedures

With the data measured as above, we can run our program to obtain estimated adsorption parameters. The program uses the one-dimensional steam flow simulator 'Adsorption' as a subroutine to simulate the transient experiment. With a pair of guessed parameters of **A** and B, the subroutine 'Adsorption' calculates the transient steam pressure. This simulated result is then compared with experimental result. If they are different, nonlinear regression is employed by calling subroutine 'dumpol'. The subroutine 'dumpol' uses the polytope algorithm to minimize the difference between simulated and experimental results. At each iteration, a new set of A and B is generated to replace the old one and is used to run the subroutine 'Adsorption' again. This procedure repeated until a good match between simulated and experimental results is achieved. **A** list of the program is included in the appendix. For more detail about the subroutine 'dumpol' please see User's Manual of FORTRAN Subroutines for Mathematical Applications (IMSL).

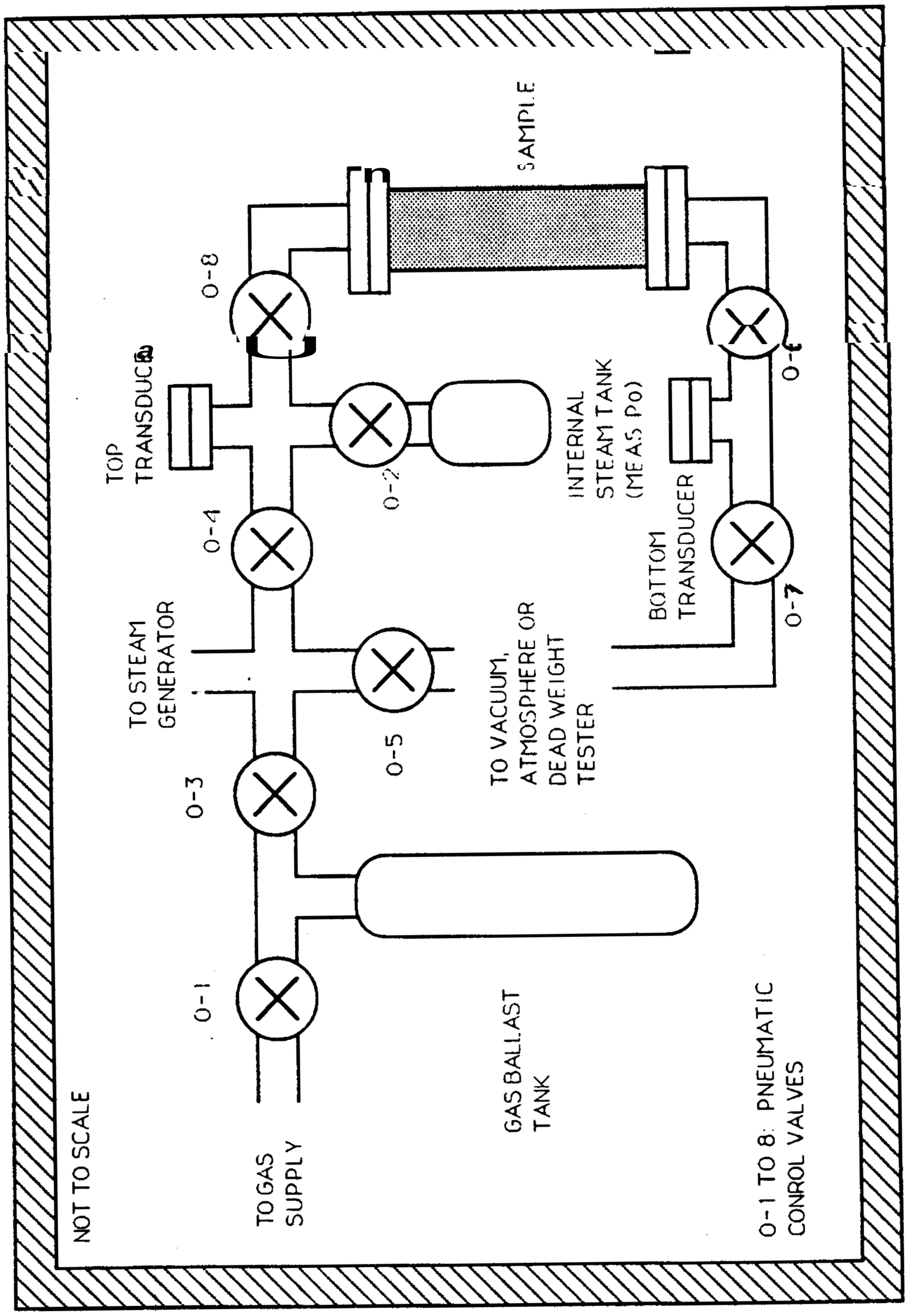

Figure **3.1:** Schematic Diagram of Experimental System Setup

Chapter 4

Results and Discussions

4.1 Experimental Results

All runs are under the same temperature conditions that Michael Harr used in his runs(125 °C) so that we could compare some of our data with Michael Harr's data for the purpose of checking and analyzing. No higher temperature were used in the fear that excessive heating would cause the o-rings in the pneumatic valves located inside the oven to acquire a permanent set and thus cause the leakage problems as noted in Michael Harr's report **(1991).** The eight experiment results are shown in Figure **4.1** through Figure **4.8.** The corresponding isotherms estimated from the experiments are shown in Figure **4.9** through Figure **4.16.**

4.2 Comparison of the Results

All results showed more or less similar pressure decline curves on a semilog plot. Some of the results are compared with Michael Harr's results. They are shown in Figures **4.17, 4.18,** and **4.19.** There are pressure differences between some of our results and Michael Harr's results. As shown in Figures **4.17** and **4.19,** the starting relative pressures are much lower than that of Michael Harr's results. This was probably caused by using different sample holders in case of Figure **4.19.** Two sample holders were used by Michael Harr: one is 2.362 centimeters in diameter and **31.7** centimeters in length and another is 1.727 centimeters in diameter and 30.63 centimeters in length. There is a short tube connecting the sample holder and pressure transducer with a valve in between. Every time we measured the steam pressure, we evacuated the tube first and then opened the valve. Thus part of steam flowed from sample into this short empty tube. This lowered the steam pressure inside the sample holder. When the large sample holder was used (Michael Harr's case), this effect was not significant. However for the small sample holder, the space inside the empty tube was relatively large compared with the space inside the sample itself. When the valve opened, a relatively large amount of steam flowed out of the sample to fill the empty space and the pressure drop was more severe than in large sample holder case. This resulted in the relative pressure difference because the saturated vapor pressures were same. Figure 4.18 shows another pair of results. The two results were more comparable because the same sample holder was used. As in the case in Figure 4.17, the difference was caused by the measuring error. The data in Michael Harr's report (1991) showed the pressures of atmosphere recorded after the run were 1.2365 bars at top of the sample holder and 0.6022 bars at the bottom of the sample holder. Which is clearly an error.

To check the validity of the isotherm estimation method, we need to compare the results obtained by regression with the results obtained from experiment. There are not many results available for the comparison. The only data available is the isotherm measured from equilibrium experiment by Shang (1992). The same rock sample was used in both transient and equilibrium experiments. The two results are plotted together in Figure 4.20. The curves have very similar shape and the data are reasonably close to each other. This is an encouraging sign.

There are many factors that affect the result of the transient flow experiment, such as the temperature, the permeability, the porosity, particle size distribution, and the sample rocks used, etc. The effects of permeability and porosity are discussed below. All other effects are considered have less effect on the results of this experiment and are not discussed.

4.3 Effect of Permeability

The samples were prepared by pouring the presieved sample into the sample holder with the holder being tapped to consolidate the sample as much as possible to gain the largest sample weight. Permeability is measured after each transient run.

Three types of isotherm were obtained as shown earlier in Figure **4.9,** Figure **4.11** and Figure **4.12:** straight line, convex to the pressure axis, and concave to the pressure axis. To examine the effect of permeability on the shape of the isotherms, different permeabilities were used to do the nonlinear regression. The results are shown in Figures **4.21, 4.22** and **4.23.** From these figures we can see that although permeability has a great effect on the numeric value of estimated isotherm, its variation does not change the shape of the isotherm curve. This means that even when there is an error in permeability or when there is no accurate permeability data available, we can still use this method to do the estimation and obtain a consistent shape of the isotherm curve.

4.4 Effect of Porosity

Porosities are calculated by knowing the volume of the sample holder and the weight of the samples. In all calculations, a value of **2.70** gram per cubic centimeter is used. To check the effect, the program were run by using different porosities rather than the calculated ones. Again the results show that the porosity only affects the numerical values of the isotherm being estimated but has no effect on the shape of the isotherm curves. The results of the isotherm plot using different porosities are shown in Figures **4.24, 4.25** and **4.26.**

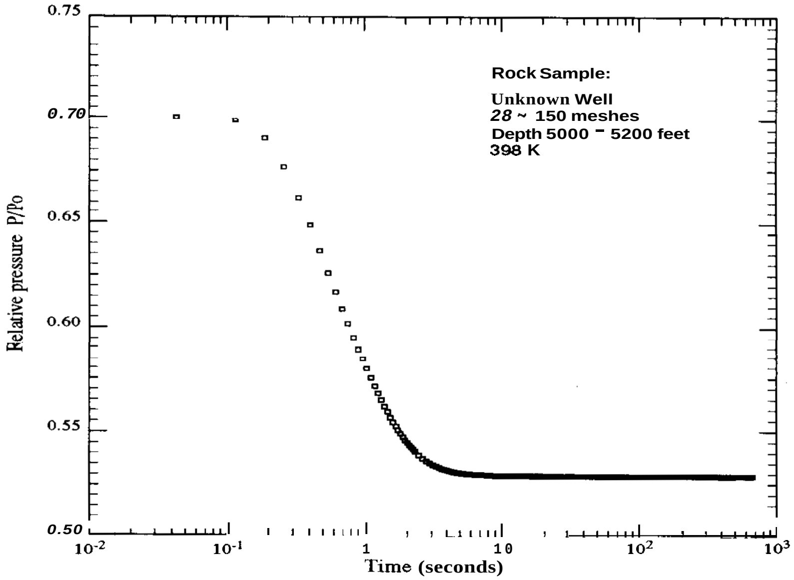

Figure 4.1: Pressure Transient Experiment Result - Geysers Shallow Reservoir

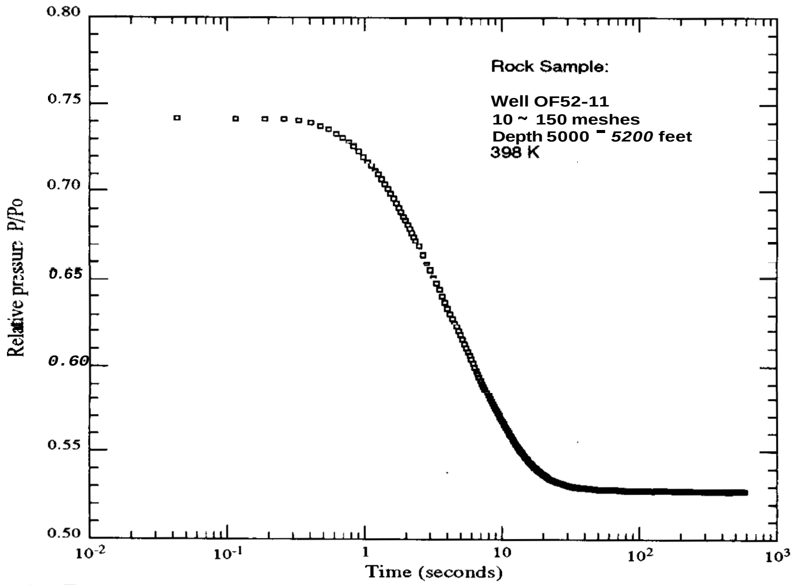

Figure 4.2: Pressure Transient Experiment Result - Geysers Geothermal Field

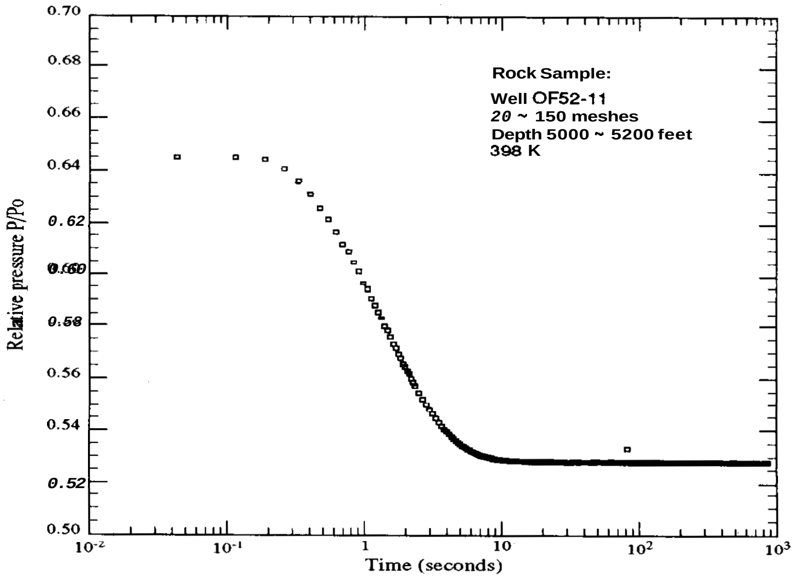

Figure 4.3: Pressure Transient Experiment Result - Geysers Geothermal Field

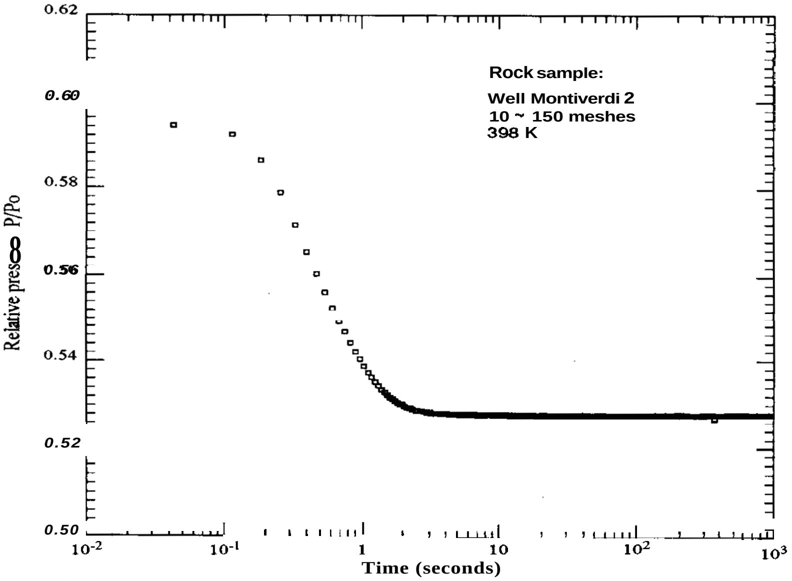

Figure 4.4: Pressure Transient Experiment Result - Montiverdi, Italy

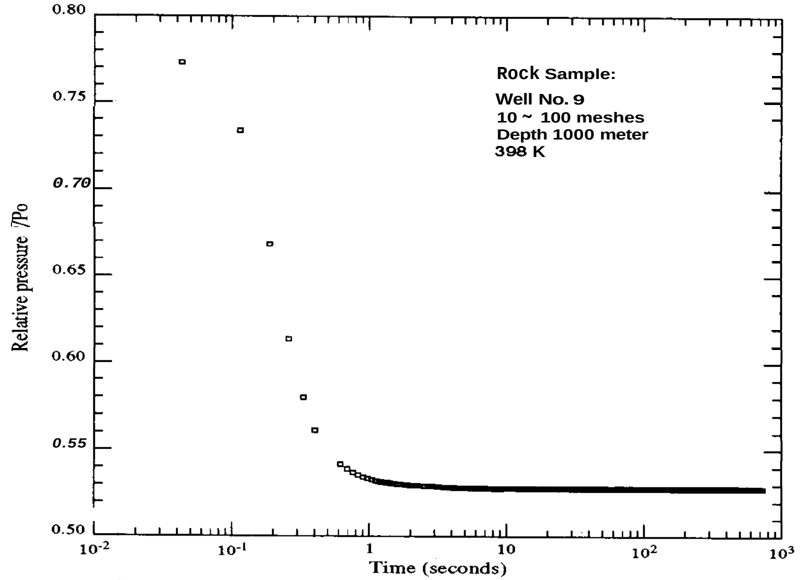

Figure 4.5: Pressure Transient Experiment Result - Reykjanes, Iceland

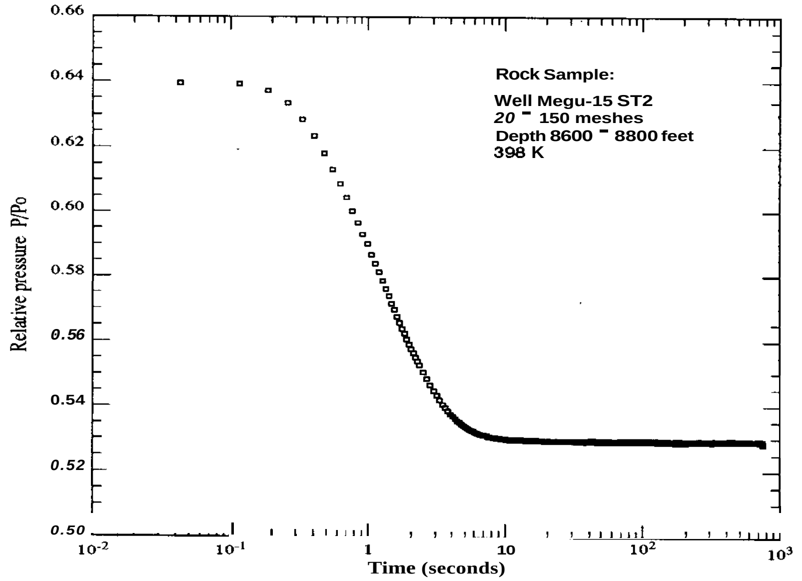

Figure 4.6: Pressure Transient Experiment Result - Geysers Geothermal Field

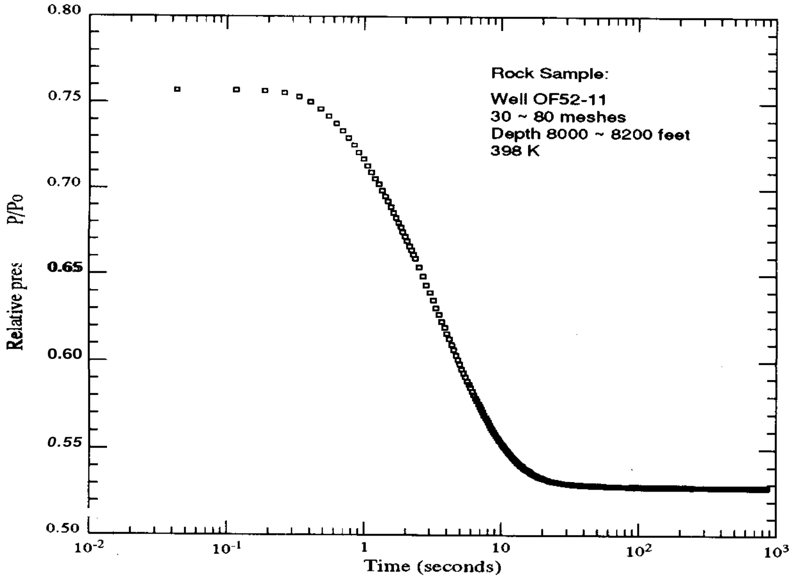

Figure 4.7: Pressure Transient Experiment Result - Geysers Geothermal Field

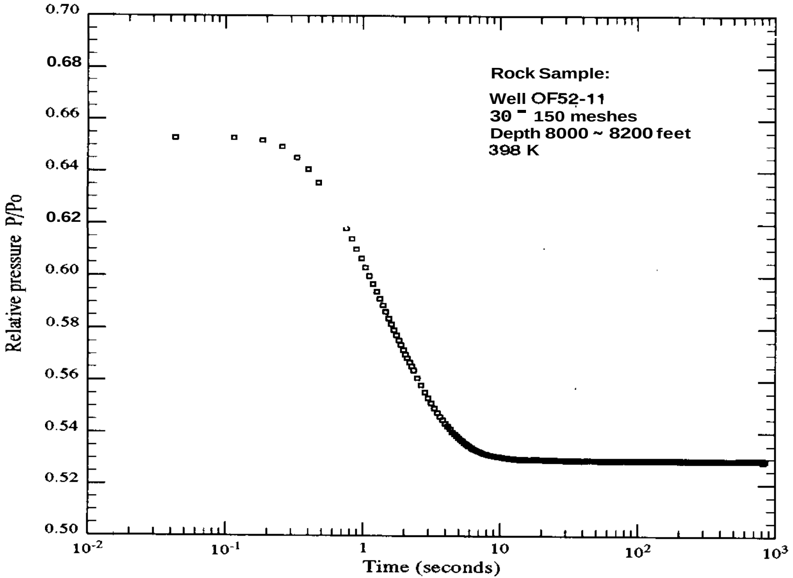

Figure 4.8: Pressure Transient Experiment Result - Reykjanes, Iceland

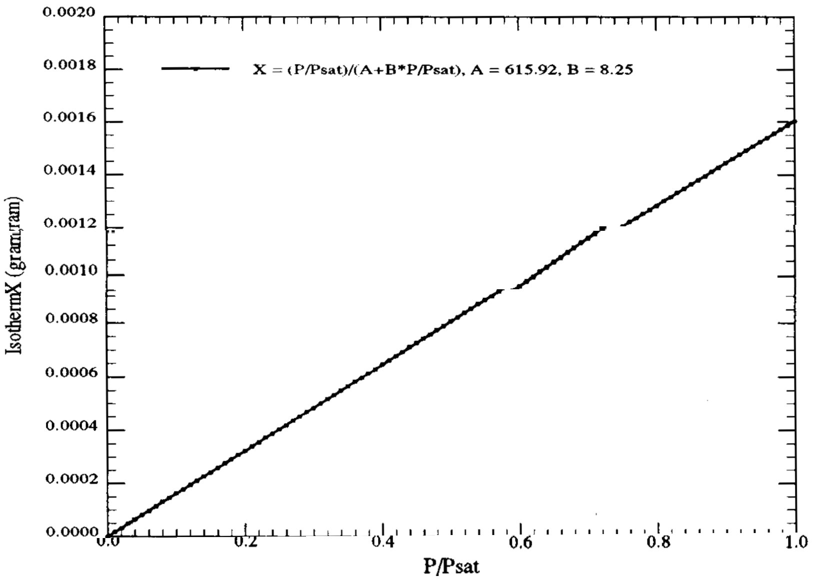

Figure 4.9: Geysers Unknown Well, Depth 5000 - 5200 Feet, 28-150 Mesh

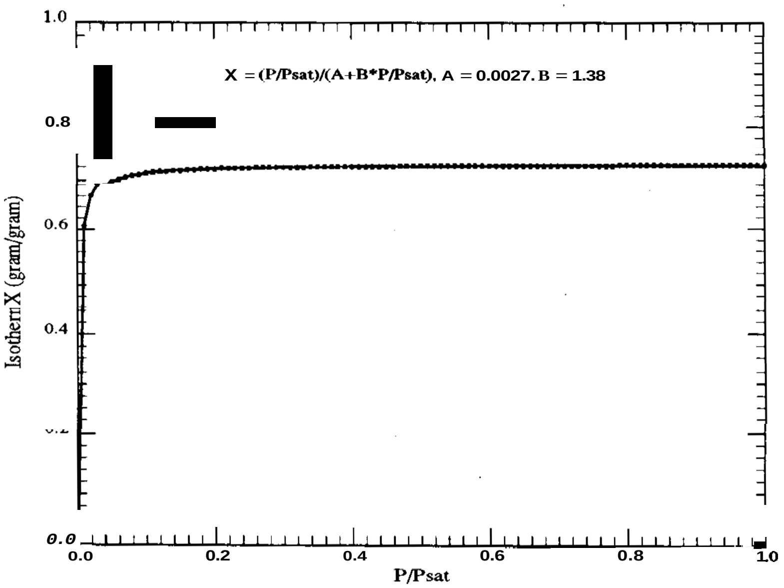

Figure 4.10: Geysers Well OF52-11, Depth 5000 - 5200 Feet, 10-150 Mesh

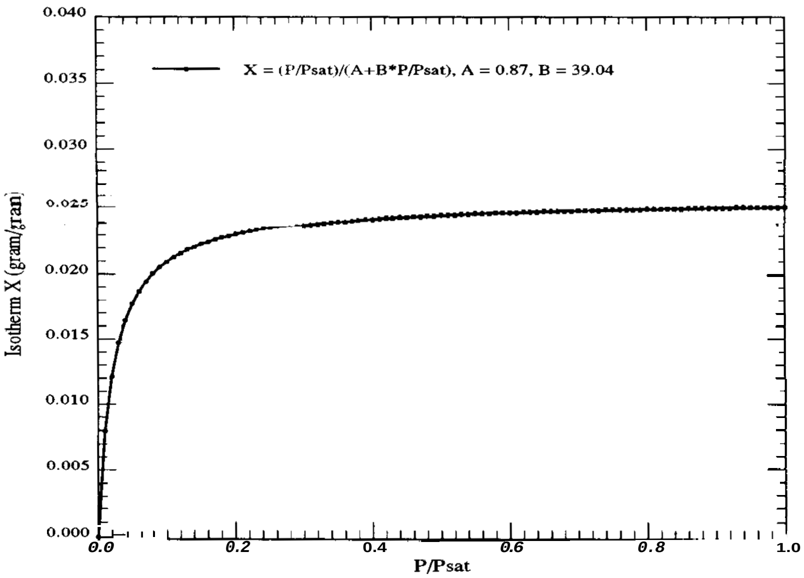

Figure 4.11: Geysers Well OF52-11, Depth 5000 - 5200 Feet, 20-150 Mesh

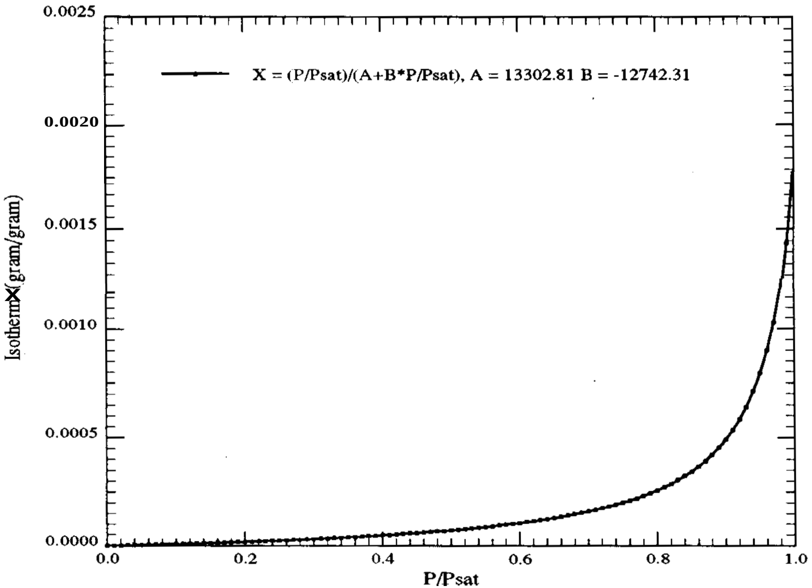

Figure 4.12: Montiverdi Well No.2, 10-150 Mesh

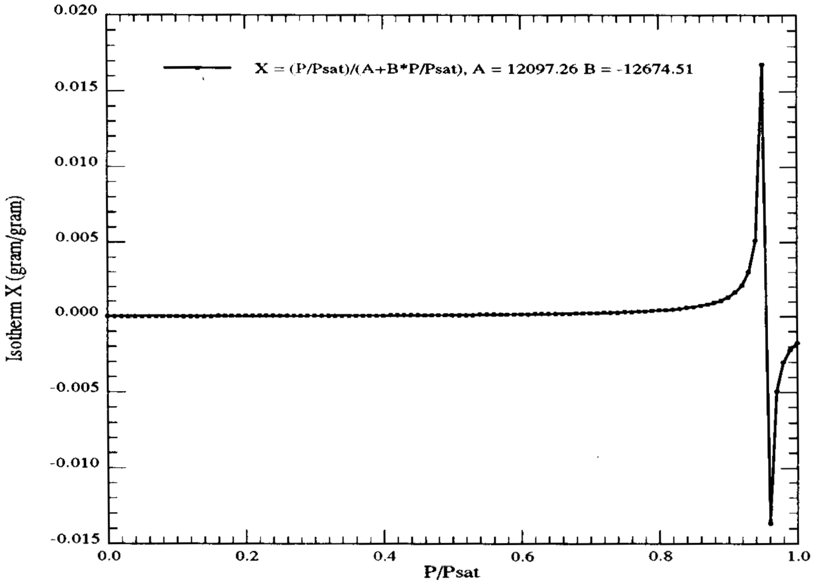

Figure **4.13:** Reykjanes Well No.9, 10-100 Mesh

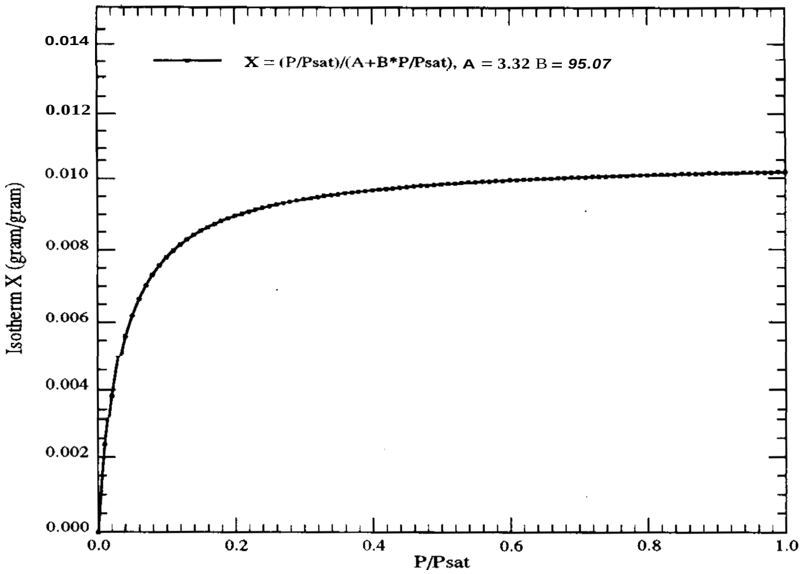

Figure **4.14:** Geysers Well Megu-15 ST2, Depth 8600 - 8800 Feet, 20-150 Mesh

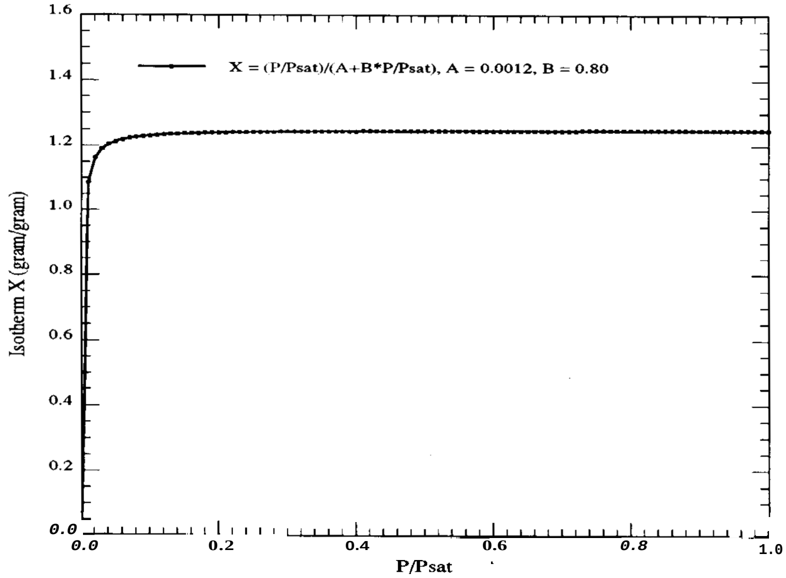

Figure 4.15: Geysers Well OF52-11, Depth 8000 - 8200 Feet, 30-80 Mesh

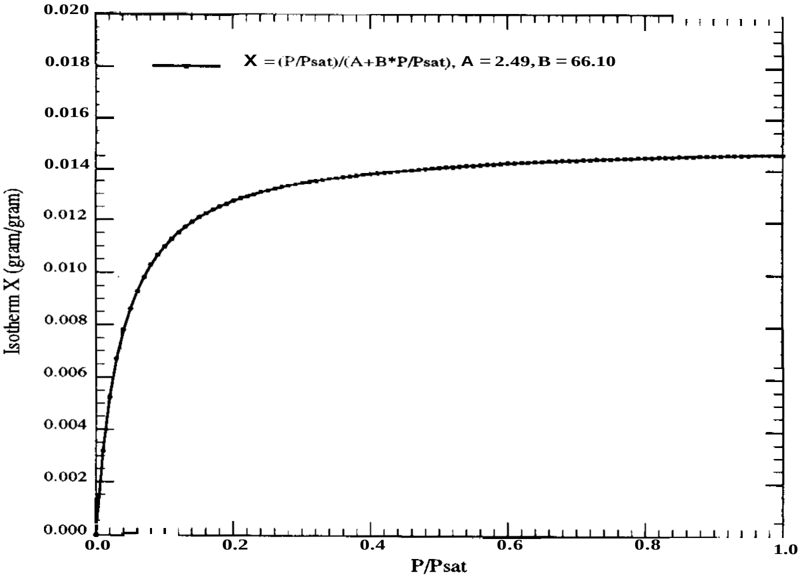

Figure 4.16: Geysers Well OF52-11, Depth 8000 - 8200 Feet, 30-150 Mesh

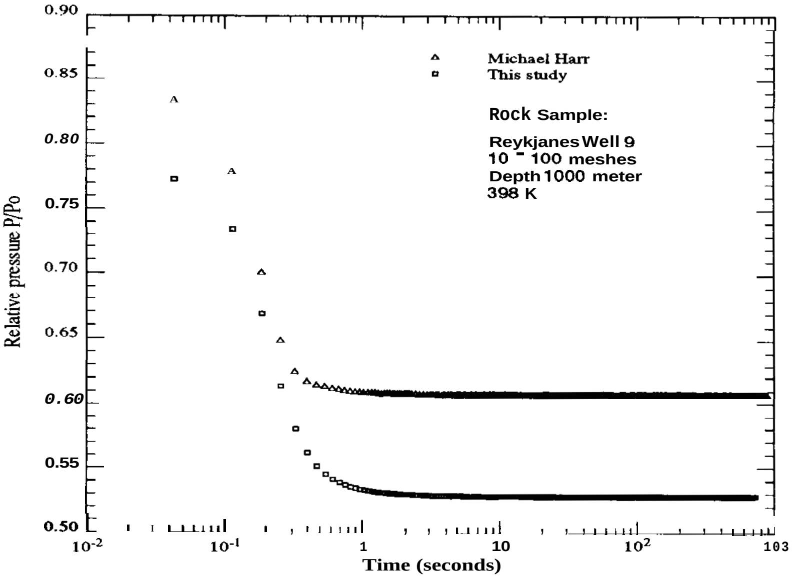

Figure 4.17: Compare of the Experiment Results - Reykjanes Well 9

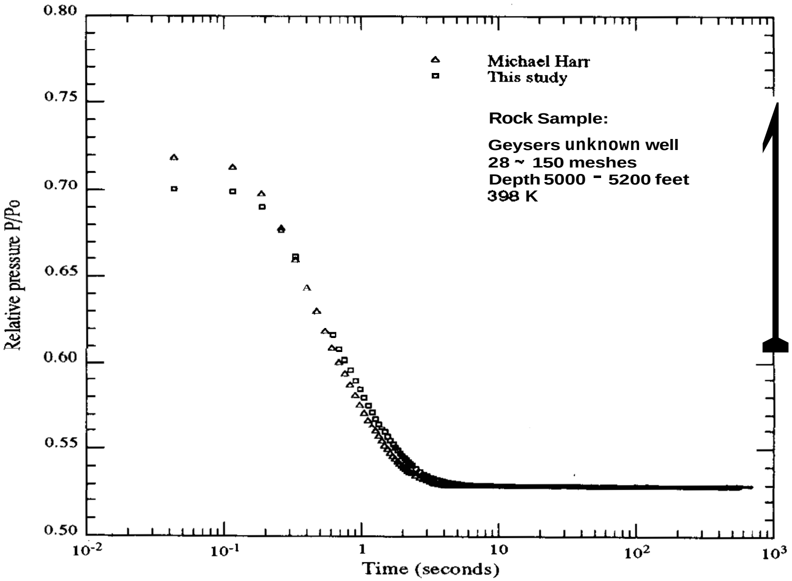

Figure 4.18: Compare of the Experiment Results - Geysers Well Unknown

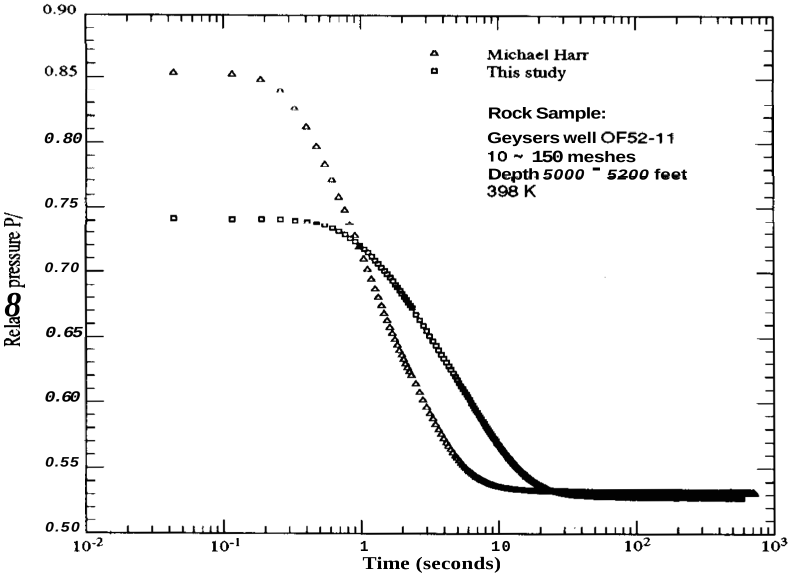

Figure 4.19: Compare of the Experiment Results - Geysers Well OF52-11

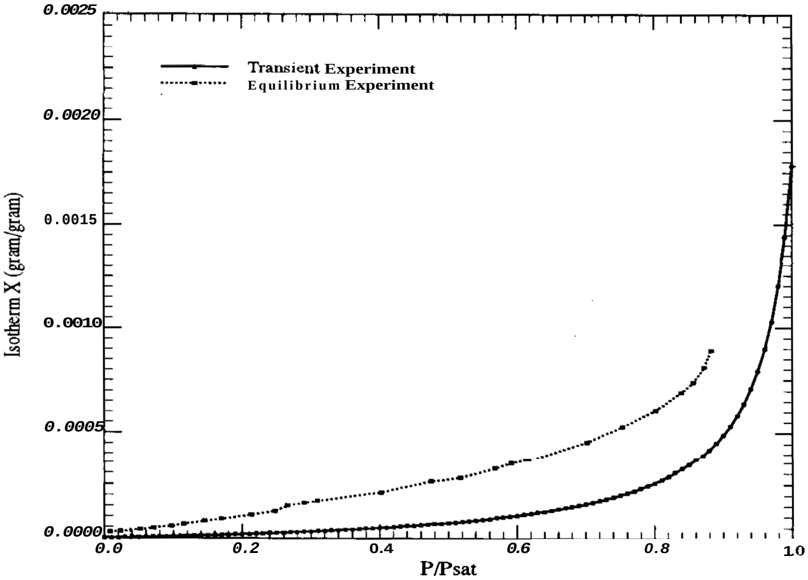

Figure 4.20: Isotherms from Different Experiments - Montiverdi 2

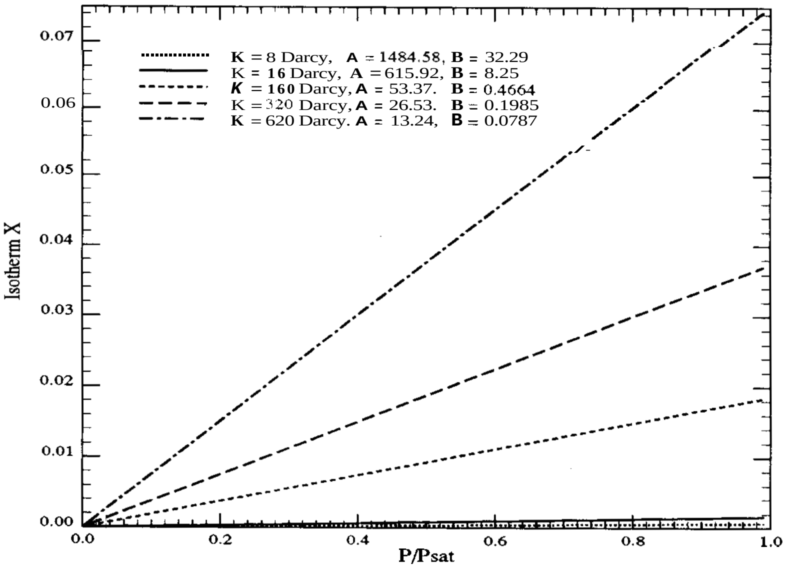

Figure 4.21: Effect of Different Permeablity - Geysers Unknown Well

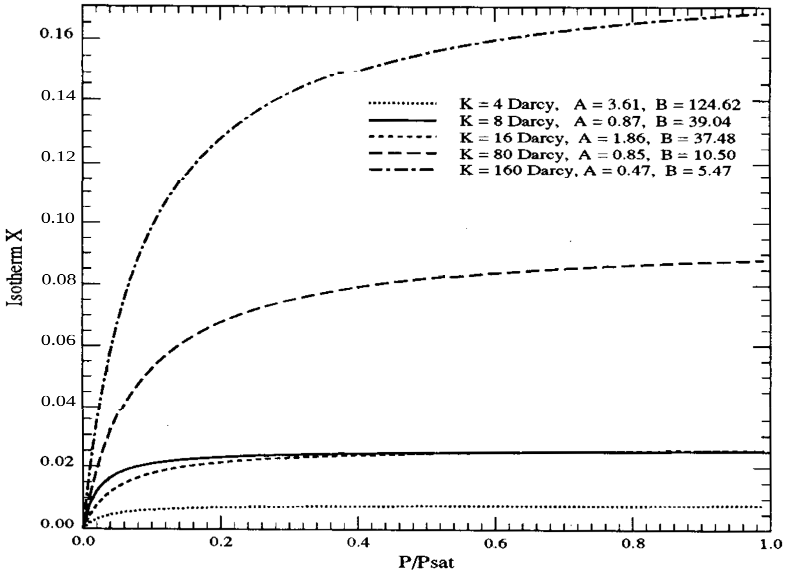

Figure 4.22: Effect of Different Permeablity - Geysers Well OF52-11

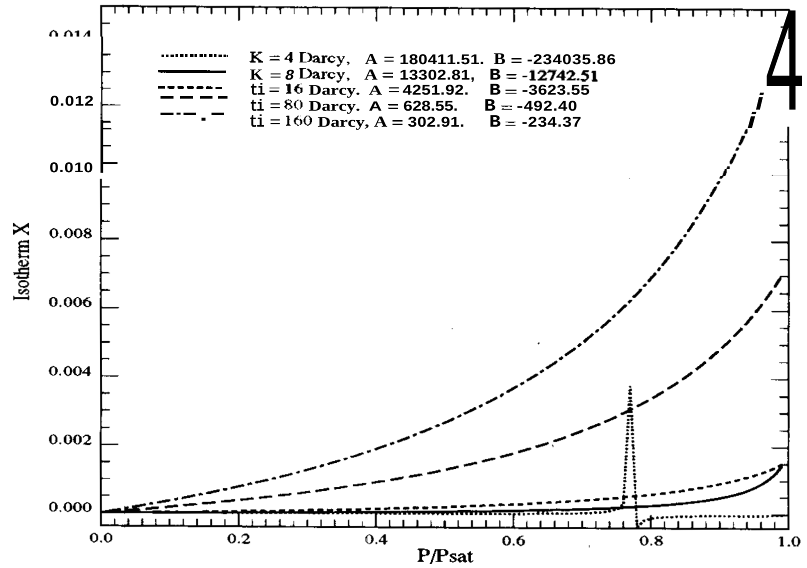

Figure 4.23: Effect of Different Permeablity - Well Montiverdi 2

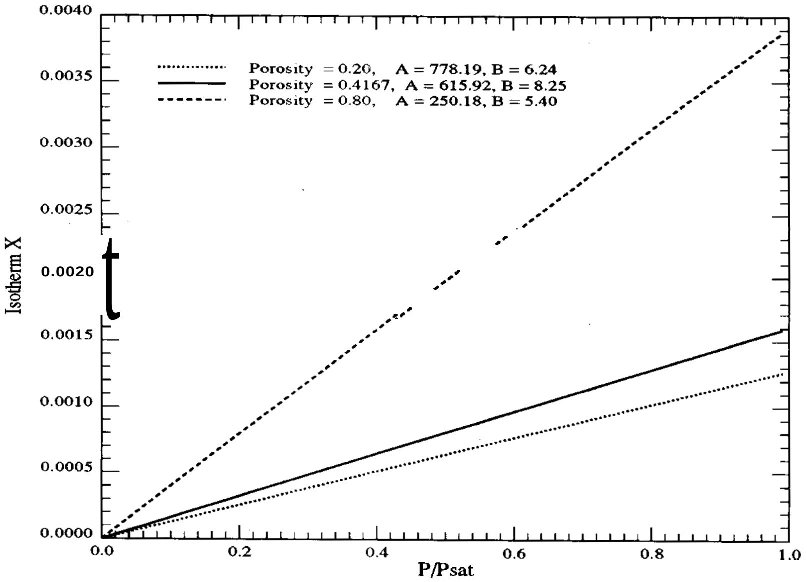

Figure 4.24: Effect of Different Porosity - Geysers Unknown Well

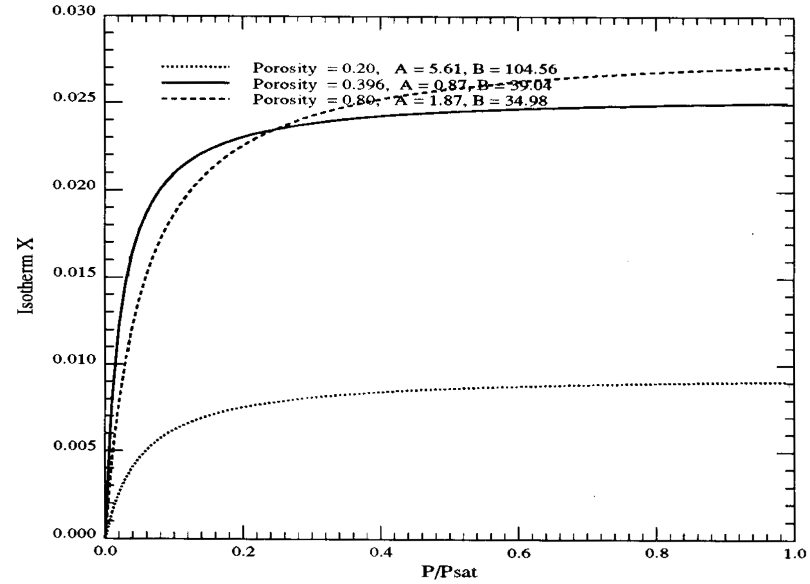

Figure 4.25: Effect of Different Porosity - Geysers Well OF52-11

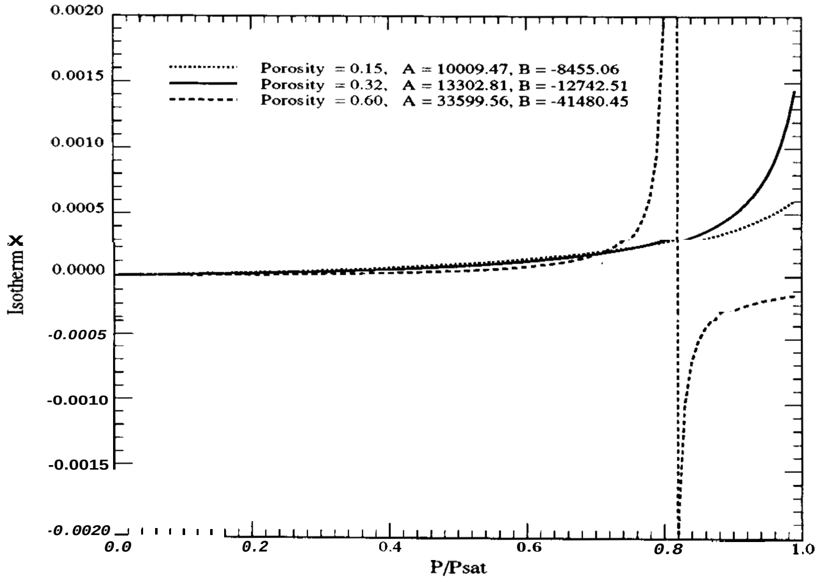

Figure 4.26: Effect of Different Porosity - Well Montiverdi 2

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

- By running the one-dimensional steam flow simulator developed by Nghiem and Ramey (1991) combined with a nonlinear regression technique, the Langmuir isotherm parameters can be estimated by using the pressure transient experiment data.
- The permeability value used in the analysis does not affect the estimated shape of the isotherm curve.
- The porosity value used in the analysis does not affect the estimated shape of the isotherm curve.
- The shape of the Langmuir isotherm curve depends heavily on the type of rock used.
- Particle size seems to have little effect on adsorption/desorption.

5.2 Recommendations

- The initial vapor pressure inside the sample holder is sensitive to the temperature changes in any part of the system. Great care must be taken to keep the temperature as stable as possible.
- The experimental procedures need to be modified in order to minimize the effects of the open space between the ends of the sample holder and the pressure transducers.
- Whenever possible in the future, a larger sample holder should be used.
- The one-dimensional simulator used only considered mass balance for simplicity. An energy balance needs to be added to the model.
- The experiments were all carried out at 125 degree C. Running experiments at different temperatures in the future will enable us to examine the temperature effect on the adsorption isotherm.

6. Nomenclature

a = equal distance between wells in x direction

A = constant

b = equal distance between wells in y direction

B = constant

C = constant

C_D = dimensionless wellbore storage coefficient

p = gas or vapor pressure

p^* = saturated vapor pressure

P = gas or vapor pressure

P_0 = saturated vapor pressure

P_{sat} = saturation pressure

P_v = steam pressure

R = relative vapor pressure function

S = water saturation

T = absolute temperature

X = isotherm

σ = experimental constant

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Appendix

```
c       Program Estimate.f
c
c       This program estimates the two parameters used in the
c       Langmuir isotherm equation. It calls the subroutine
c       Adsorption to simulate the transient experiment and
c       compares the result with true experimental data. Then
c       it calls subroutine dumpol to do nonlinear regression
c       to give the two estimated 'best' values.
c       The subroutine dumpol minimizes a function of N variables
c       using a direct search polytope algorithm.
c       The experimental data file should be 'exp.dat' and
c       the simulated result file should be 'simu.dat'.
c       User must specify the number of experiment data 'n'.
c
        implicit double precision (A-H,O-Z)
        integer i,m,n,k,nn,maxfcn,nout
        parameter (n=450,nn=2, m=150)
        dimension t(n),tsimu(m),p(n),pdata(m),psimu(m),
     *            x(nn),xguess(nn)
        external fcn,umach,dumpol
        xguess(1)=10.
        xguess(2)=10.
        call Adsorption(xguess)
        open(UNIT = 8, STATUS = 'OLD', file='exp.dat')
        rewind 8
        do 100 k=1,n
        read(8,*) junk1,t(k),junk2,p(k)
100     continue
        close(8)
        open(UNIT = 9, STATUS = 'OLD', file='simu.dat')
        rewind 9
c
c       File 'new.dat' is used to store the interpolation results.
c       If 'new.dat' already existed, change the status to 'old'.
c
        open(UNIT = 7, STATUS = 'NEW', file='new.dat')
        rewind 7
        do 300 i=1,m
        read(9,*) tsimu(i),psimu(i)
        k=1
200     if(tsimu(i) .lt. t(1) ) then
        pdata(i)=p(1)
        write(7,*) tsimu(i),pdata(i)
        goto 300
        elseif(tsimu(i) .gt. t(n)) then
        pdata(i)=p(n)
        write(7,*) tsimu(i),pdata(i)
        goto 300
        elseif(tsimu(i) .gt. t(k)) then
```

```
      k=k+1
      goto 200
      endif
      pdata(i)=p(k-1)
    *        +(p(k)-p(k-1))*(tsimu(i)-t(k-1))/(t(k)-t(k-1))
      write(7,*) tsimu(i),pdata(i)
300   continue
      close(9)
      close(7)
      ftol=1.0e-8
      maxfcn=800
      sss=1.0
      call dumpol(fcn,nn,xguess,sss,ftol,maxfcn,x,fvalue)
      call umach(2,nout)
      write(nout,400) (x(k),k=1,nn),fvalue
400   format ('   The best estimate for the minimum value of the',/,
    *         '   function is x=( '2(2x,f14.8),')' ,/,
    *         '   with function value fvalue= ',e12.6)
      end
c
c     Define function to be minimized.
c
      subroutine fcn(n,x,f)
      implicit double precision (a-h,o-z)
      integer n,m
      parameter(m=150)
      dimension x(n),psimu(m),pdata(m)
      call Adsorption(x)
      open(UNIT = 9, STATUS = 'OLD', file='simu.dat')
      rewind 9
      open(UNIT = 7, STATUS = 'OLD', file='new.dat')
      rewind 7
      f=0.
      do 100 i=1,m
      read(9,*) t,psimu(i)
      read(7,*) tsimu,pdata(i)
      f=f+(psimu(i)-pdata(i))**2
100   continue
      close(9)
      close(7)
      write(*,*)x,f
      return
      end
c
c     This program was originally written by Nghiem, C.P.
c     and Ramey, H.J. Jr.. See Reference [22] for details.
c     Modified parts were written in lower case.
c
      subroutine Adsorption(xx)
      implicit double precision (A-H,0-Z)
     INCLUDE 'M1.CMM'
```

```
      INCLUDE 'M2.CMM'
      INCLUDE 'M3.CMM'
      INCLUDE 'M4.CMM'
      INCLUDE 'M5.CMM'
      INCLUDE 'M6.CMM'
      INCLUDE 'M7.CMM'
       dimension xx(2)
C OUTPUT FILE
       open(UNIT = 9, STATUS = 'OLD', file='simu.dat')
       rewind 9
C OUTPUT FORMAT
       IPRESS=2
       ITIME=1
C STEAM
       WM= 18.015D0
       R=  8.313E07
c To be modified according to experiment conditions
       DSTW= 0.9589D0
c Temperature (Kelvin)
       TP= 394.177D0
c Steam charge pressure (dyne/cm^)2
       PINIT=1338500.
c Saturated vapor pressure of water (dyne/cm^2)
       PSAT=2050140.
c Outlet pressure (Atmospheric pressure) (dyne/c^2)
       POUT=1085240.
c Rock density (gm/cm^3)
       RHOR= 2.700D0
c Porosity of the sample
       PHI=0.4048
c Permeability of the sample (darcy)
       XK=7.00
       XK=9.8697E-9*XK
c Length of the sample (cm)
       XL=30.63
c Simulate time
       TIME=300.
c Two parameters used in the Langmuir equation
       AA=xx(1)
       BB=xx(2)
C NUMERICAL MODEL
      IADS=1
      IC= 0
      XMF= 1.
      N= 201
      DT=0.01
      DX= XL/200.D0
      WGT= 1.
      STIME= 0.
      XMSH(1)= 0.
      DO 666 I= 2,201
```

```
666   XMSH(I)= XMSH(I-1)+DX
      PRI= 0.01D0
      CONVG= 1.
      CALL INPUT
      CALL TABLE
      CALL INIT
      ITER= 0
1000  CALL NEWDAT
2000  CALL COMPUT
      CALL CHECK
      IF (CONVG.NE.1.) THEN
        ITER= ITER+1
        GOTO 2000
      ENDIF

      STIME= STIME+DT

      IF (ITIME .EQ. 1) THEN
        PRINTM=STIME
      ELSE
        PRINTM=STIME/60.D0
      ENDIF

      IF (IPRESS .EQ. 1) THEN
        PRINPR=PI(201)/10000.D0
      ELSEIF (IPRESS .EQ. 2) THEN
        PRINPR=PI(201)/1000000.D0
      ELSE
        PRINPR=PI(201)/PSAT
      ENDIF
        write(9,*) PRINTM,PRINPR
      CONVG= 1.
      ITER= 0
      DT=1.05*DT
      IF (STIME.LE.TIME) GO TO 1000
        close(9)
        return
      END


      SUBROUTINE INPUT

        implicit double precision (A-H,0-Z)
      INCLUDE 'M1.CMM'
      INCLUDE 'M2.CMM'


C READ P,v,VISCOSITY DATA. COMPUTE Z AND CG FACTORS.
C INPUT: P(psia),V(ft3/lbm),VISC(cpoise)
```

```
      OPEN(UNIT = 7, STATUS = 'OLD', FILE='steam.inp')

      DO 10 I= 1,51
         READ (7,200) PR(I), VL(I), VIC(I)
         P(I)= PR(I)*6.894757E04
         V(I)= VL(I)*62.428D0
         VISC(I)= VIC(I)*0.01D0
 10   CONTINUE
      CLOSE (7)
200   FORMAT (3F14.4)
      RETURN
      END

      SUBROUTINE TABLE

        implicit double precision (A-H, O-Z)
      INCLUDE 'M1.CMM'
      INCLUDE 'M2.CMM'
      INCLUDE 'M3.CMM'

      DO 11 I= 1,51
         Z(I)= WM*P(I)*V(I)/(R*TP)
         DST(I)= 1./V(I)
         IF(I.GE.2) THEN
              DDST(I)= DST(I)-DST(I-1)
              DP(I)= P(I)-P(I-1)
              CG(I)= DDST(I)/(DST(I)*DP(I))
         ENDIF
 11    CONTINUE

C   COMPUTE M(P)

       DO 12 I= 1,51
         PMUZ(I)= P(I)/(VISC(I)*Z(I))
         IF(I.GE.2) THEN
             AVG(I)= 0.5*(PMUZ(I-1)+PMUZ(I))
             DPAVG(I)= DP(I)*AVG(I)
             IF (I.EQ.2) THEN
                XM(I)= DPAVG(I)
             ELSE
                XM(I)= XM(I-1)+DPAVG(I)
             ENDIF
         ENDIF
 12    CONTINUE
       RETURN
       END

      SUBROUTINE INIT

        implicit double precision (A-H, O-Z)
      INCLUDE 'M1.CMM'
```

```
      INCLUDE 'M2.CMM'
      INCLUDE 'M3.CMM'
      INCLUDE 'M4.CMM'
      INCLUDE 'M5.CMM'

C  INITIALIZE. FIND CORRESPONDING Z, VISCOSITY AND CG

      DO 13 I= 1,201
         IF(I EQ.1) THEN
           IF(IC.EQ.0) THEN
              PI(I)= POUT
           ELSE
              PI(I)= PINIT
           ENDIF
         ELSE
           PI(I)= PINIT
         ENDIF
 13   CONTINUE
      PO= PI(201)
      P1= PI(1)
      DO 91 I= 2,51
        PP(I-1)= P(I)
        XMM(I-1)= XM(I)
        CGG(I-1)= CG(I)
 91   CONTINUE
      RETURN
      END

      SUBROUTINE NEWDAT

        implicit double precision (A-H, O-Z)
      INCLUDE 'M1.CMM'
      INCLUDE 'M2.CMM'
      INCLUDE 'M3.CMM'
      INCLUDE 'M4.CMM'
      INCLUDE 'M5.CMM'


C KLINKERBERG EFFECT

      SP= 0.
      DO 5 I= 1,201
 5    SP= SP+PI(I)
      PN= SP/201.
      XKK= XK*(1.+1.4E05/PN)
      DO 30 K= 1,201
       IF(STIME.EQ.0.) THEN
            CALL TABSEQ(PP,XMM,50,PI(K),XMI(K))
       ELSE
         IF(IC.EQ.0) THEN
            IF(K.GE.2.AND.K.LE.201) XMI(K)= XMN(K)
```

```
          ELSE
             XMI(K)= XMN(K)
          ENDIF
        ENDIF
        CALL TABSEQ(P,VISC,51,PI(K),VISCI(K))
        CALL TABSEQ(P,Z,51,PI(K),ZI(K))
        CALL TABSEQ(PP,CGG,50,PI(K),CGI(K))
 30   CONTINUE
      RETURN
      END

      SUBROUTINE COMPUT

        implicit double precision (A-H,O-Z)

      INCLUDE 'M1.CMM'
      INCLUDE 'M2.CMM'
      INCLUDE 'M3.CMM'
      INCLUDE 'M4.CMM'
      INCLUDE 'M5.CMM'
      INCLUDE 'M6.CMM'
      INCLUDE 'M7.CMM'

C  COMPUTE MATRIX COEFFICIENT

      DO 17 I= 1,201
          X(I)= PI(I)/(AA*PSAT+BB*PI(I))
          DXDP(I)= AA*PSAT/(AA*PSAT+BB*PI(I))**2
          A1(I)= PHI*WM*VISCI(I)*CGI(I)
     *          *(1.-X(I)*RHOR*(1.-PHI)/(DSTW*PHI))
          A2(I)= -DXDP(I)*(1.-PHI)*VISCI(I)*RHOR*WM/DSTW
          IF(CONVG.EQ.1.) THEN
            A3(I)= DXDP(I)*ZI(I)*R*VISCI(I)*TP*RHOR*(1.-PHI)
     *            /PI(I)
          ENDIF
        A(I)= A1(I)+A2(I)+A3(I)
17     CONTINUE
       B= XKK*WM
       IF(IC.EQ.1) THEN
          DO 177 I= 1,201
            IF(I.EQ.l) THEN
              D1(I)= 1.+2.*B*WGT*DT/(A(I)*DX**2)
              U1(I)= -2.*B*WGT*DT/(A(I)*DX**2)
              S1(I)= 2.*B*DT*R*TP*XMF/(A(I)*DX*WM)
     *             +(1.-2.*B*(1.-WGT)*DT/(A(I)*DX**2))*XMI(I)
     *             +2.*B*(1.-WGT)*DT*XMI(I+1)/(A(I)*DX**2)
            ELSEIF(I.EQ.201) THEN
              D1(I)= 1.+2.*B*WGT*DT/(A(I)*DX**2)
              T1(I)= -2.*B*WGT*DT/(A(I)*DX**2)
              S1(I)= (1.-2.*B*(1.-WGT)*DT/(A(I)*DX**2))*XMI(I)
     *              +2.*B*(1.-WGT)*DT*XMI(I-1)/(A(I)*DX**2)
```

```
            ELSE
              D1(I)= 1.+2.*B*WGT*DT/(A(I)*DX**2)
              T1(I)= -WGT*B*DT/(A(I)*DX**2)
              U1(I)= T1 (I)
              S1(I)= B*(1.-WGT)*DT*(XMI(I+1)+XMI(I-1))/(A(I)*DX**2)
     *               +XMI(I)*(1.-2.*B*(1.-WGT)*DT/(A(I)*DX**2))
            ENDIF
 177     CONTINUE
         CALL THOMAS(1,201,T1,D1,U1,S1)
         DO 81 I= 1,201
 81      XMN(I)= S1 (I)
       ELSE
         DO 188 I= 2,201
          IF (I.EQ.2) THEN
            DI(I-1)= 1.+2.*B*WGT*DT/(A(I)*DX**2)
            U(I-1)= -B*WGT*DT/(A(I)*DX**2)
            S(I-1)= B*DT*XMI(I-1)/(A(I)*DX**2)
     *              +B*(1.-WGT)*DT*XMI(I+1)/(A(I)*DX**2)
     *              +(1.-2.*B*(1.-WGT)*DT/(A(I)*DX**2))*XMI(I)
          ELSEIF(I.EQ.201) THEN
            DI(I-1)= 1.+2.*B*WGT*DT/(A(I)*DX**2)
            T(I-1)= -2.*B*WGT*DT/(A(I)*DX**2)
            S(I-1)= (1.-2.*B*(1.-WGT)*DT/(A(I)*DX**2))*XMI(I)
     *               +2.*B*(1.-WGT)*DT*XMI(I-1)/(A(I)*DX**2)
          ELSE
            DI(I-1)= 1.+2.*B*WGT*DT/(A(I)*DX**2)
            T(I-1)= -WGT*B*DT/(A(I)*DX**2)
            U(I-1)= T(I-1)
            S(I-1)= B*(1.-WGT)*DT*(XMI(I+1)+XMI(I-1))/(A(I)*DX**2)
     *              +XMI(I)*(1.-2.*B*(1.-WGT)*DT/(A(I)*DX**2))
          ENDIF
 188      CONTINUE
          CALL THOMAS(1,200,T,DI,U,S)
          DO 90 I=1,200
             XMN(I+1)= S(I)
 90       CONTINUE
       ENDIF

C  NEW PRESSURE IN CORE

      IF(IC.EQ.0) THEN
         NI= 2
      ELSE
         NI= 1
      ENDIF
      DO 40 I= NI,201
         CALL TABSEQ(XMM,PP,50,XMN(I),PI(I))
 40   CONTINUE
      DO 41 I= NI,201
         CALL  TABSEQ(P,DST,51,PI(I),DSTO(I))
 41   CONTINUE
```

```
      RETURN
      END

      SUBROUTINE CHECK

        implicit double precision (A-H, O-Z)
      INCLUDE 'M1.CMM'
      INCLUDE 'M2.CMM'
      INCLUDE 'M3.CMM'
      INCLUDE 'M4.CMM'
      INCLUDE 'M5.CMM'
      INCLUDE 'M6.CMM'
      INCLUDE 'M7.CMM'

      DO 1 I= 1,201
        PCK(I)= PSAT*AA*X(I)/(1.-BB*X(I))
        SS(I)= (X(I)*RHOR*(1.-PHI))/(DSTW*PHI)
 1    CONTINUE
      CONVG= 1.
      DO 2 I= 1,201
        IF(ABS(PI(I)-PCK(I)).GT.100000.) THEN
           CONVG= CONVG+1.
           CALL TABSEQ(P,DST,51,PCK(I),DSTAR(I))
           A3(I)= A3(I)+PHI*(1.-SS(I))*(DSTAR(I)-DSTO(I))/DT
           IF(I.GE.2) XMI(I)= XMN(I)
        ELSE
           CONVG= CONVG+0.
        ENDIF
 2    CONTINUE
      RETURN
      END

C SEQUENTIAL SEARCH AND LINEAR INTERPOLATION

      SUBROUTINE TABSEQ(X,Y,N,XX,YY)

        implicit double precision (A-H, O-Z)
        dimension X(*),Y(*)

      I= 1
 100  I= 1+1
      IF(I.GT.N) GO TO 98
      IF(XX.GT.X(I)) GO TO 100
      YY= Y(I-1)+(Y(I)-Y(I-1))*(XX-X(I-1))/(X(I)-X(I-1))
      RETURN
 98   YY= Y(N)
      RETURN
      END

      SUBROUTINE THOMAS (IL,IU,BB,DD,AA,CC)
        implicit double precision (A-H, 0-Z)
```

```
        dimension AA(1),BB(1),CC(1),DD(1)

      LP= IL+1
      DO 10 I= LP,IU
      R= BB(I)/DD(I-1)
      DD(I)= DD(I)-R*AA(I-1)
   10 CC(I)= CC(I)-R*CC(I-1)
      CC(IU)= CC(IU)/DD(IU)
      DO 20 I= LP,IU
      J= IU-I+IL
   20 CC(J)= (CC(J)-AA(J)*CC(J+1))/DD(J)
      RETURN
      END
```