**TRANSIENT ADSORPTION EXPERIMENT - SALINITY AND NONCONDENSIBLE
GAS EFFECTS**

QUARTERLY REPORT

PERIOD JULY THROUGH SEPTEMBER 1993

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

**Work Performed Under Contract DE-FG07-90ID12934
For
U. S. Department of Energy
Office of Industrial Technologies
Washington, D.C.**

**By
Stanford Geothermal Program
Stanford University**

MASTER
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

402

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

RECEIVED

DEC 01 1993

OSTI

Quarterly Report for July-September 1993

Stanford Geothermal Program
Stanford University

October 20, 1993

1 TRANSIENT ADSORPTION EXPERIMENT - SALINITY AND NONCONDENSIBLE GAS EFFECTS

This experimental project is being conducted by Research Assistant Steve Palar and Profs. Roland N. Horne and Henry J. Ramey, Jr. The purpose of this project is to analyze the adsorption and desorption of steam in geothermal reservoirs, considering the effects of dissolved salts and of noncondensable gases.

During this reporting quarter, seven runs were performed. The move to our new building (Green) took place at the end of August and the transient adsorption equipment had to be disassembled prior to the moving date. The equipment has been reassembled in the new building, and will shortly be ready to run again.

One of the major features of this new series of experiments was that it used a new core holder. The new core holder is much larger in length and volume than the one used previously. The objective in increasing the core size is to slow down the rate of pressure change in the apparatus and thereby improve the resolution of the measurements. The new configuration should provide a more accurate evaluation of the adsorption isotherms.

All the seven runs used the same sample, which was obtained from the Calpine Corporation well MLM-3 located in the south of the Geysers field.

The sample was cored from 1325 m measured depth or 1320 m vertical depth. In order to fit into the equipment's sample holder, the whole core was pulverized and subsequently sieved to uniform mesh sizes of 20-45 and 45-150.

1.1 20 - 45 Mesh Size

Four runs were made using this coarser sample :

- 2 runs with steam only
- 1 run with CO₂ only
- 1 run with steam and 7.6 % CO₂

The sample porosity and permeability were measured to be 52.22 % and 37.5 darcy respectively.

The vertical axis in Figure 1 shows the pressure recorded by the top transducer, whereas the horizontal axis denotes the time elapsed after the sample bottom is exposed to atmosphere.

The drop to atmospheric pressure starts at less than one second after the sample is exposed to atmosphere. The immediate drop is due to the high permeability of the sample. Should a lower permeability sample be utilized - as in the case of the next series of experiments - the pressure drop will start at a much later time.

In order to determine the shape and the parameters of the adsorption isotherm, the transient pressure data from the two steam runs was passed into the computer program developed by Qi and Horne (1993). The program uses the adsorption subroutine created by Nghiem and Ramey (1991). Details of this program are presented in the MS thesis of Ming Qi (1993).

A complete equation for the isotherm is:

$$X = \frac{\frac{P}{P^{sat}}}{A + B \frac{P}{P^{sat}}} \quad (1)$$

where :

X denotes the weight ratio of the adsorbate (steam) to the adsorbent (rock)

P / P^{sat} represents the ratio of pressure to the saturation pressure of steam at a particular temperature.

The parameters A and B determine the shape of the isotherm.

The shapes of the isotherms from the two experiments are both concave upward, however the values of the isotherm parameters A and B are different (see Figure 2). This is not surprising since the pressure versus time curves of the two runs are not identical, but show a time shift. This time shift might be caused by a discrepancy in the quantity of steam inside the sample prior to the desorption run. The steam quantity is in turn related to the evacuating and soaking times.

Evacuating time refers to the time required to evacuate any entrapped air inside the sample prior to introducing steam. Soaking time denotes the length of time used to expose the sample with steam. A minimum of 24 hours was used for both.

Another factor which might have contributed to the shift is condensation inside the sample. Since the steam is generated inside the air bath at supposedly 125°C, a slight decrease of the temperature will condense some of the entrapped steam.

1.2 45 - 150 Mesh Size

Using this finer sample, three runs were conducted :

- 2 runs with steam only
- 1 run with steam and 19.6 % CO_2

The permeability of the sample is 0.207 darcy, which is very tight. Porosity of the sample has not been measured yet, since the sample has yet to be weighed. The weighing of the sample is pending, since another run using the same sample to confirm the results is desired. Consequently, the measurement of adsorption isotherm, which requires porosity data, is also still pending.

The graph of pressure vs desorption time for the sample is shown in Figure 3. Here also there are shifts in desorption times. However the effect is more pronounced than in the experiments using 20 - 45 Mesh size, since the shift is in the upper end of the logarithm scale.

1.3 The effects of sample size

In order to compare the effects of sample size, the steam-only runs from the two different sample sizes are shown in Figure 4.

This comparison indicates that the role of permeability is very important. The larger the permeability or the sample particle, the longer is the starting time for the desorption.

1.4 The effects of noncondensable gas

CO₂ as a noncondensable gas was used due to its existence in a typical geothermal field. It was introduced to the air-free sample under vacuum and the pressure was recorded. After some time elapsed for equilibrium, without changing the volume, steam was added to the system. The resulting pressure was the total combined pressure of both the steam and the CO₂.

A CO₂-only run was conducted, however the initial pressure used is lower than that of steam. It can be seen in Figure 1 that the pressure drop in CO₂ is not as steep as that in steam.

Experiments with steam including CO₂ at concentrations up to 20 % did not give noticeably different results compared to the steam-only runs. CO₂ occupies the largest pores by virtue of its noncondensable property.

These results are of great importance to the understanding of how adsorption will occur in actual geothermal reservoirs. The experiments show that steam adsorption in a field such as the Geysers is not affected by the presence of noncondensable gases.

1.5 Plan for the next experiments

Currently a new power outlet for the oven is being installed in the new laboratory. A valve inside the oven also is being replaced due to leaking. As soon as the equipment is ready, the experiment will start with the replicate run for the 45-150 Mesh size, followed by new runs using dissolved solids.

2 ADSORPTION OF WATER VAPOR ON RESERVOIR ROCKS

This experimental project is under the direction of Research Associate Dr. Shubo Shang, and Prof. Henry J. Ramey, Jr. The focus of the work is the experimental investigation of adsorption of water onto geothermal reservoir rocks.

Figure 1: Pressure transient experiment using 20 - 45 mesh size

Figure 2: Inferred adsorption isotherms

Figure 3: Pressure transient experiment using 45 - 120 mesh size

Figure 4: Comparison of mesh size effects

Figure 5: Isotherms on Calpine Well MLM-3 Core A

In our continued effort to collect water adsorption/desorption data on a wide range of reservoir samples, we have performed tests on samples from Calpine Co.'s well MLM-3, South Geysers field, three well cuttings from different depths of well Prati State 12, Northwest Geysers steam field. We also measured the surface area of a number of rock samples by running nitrogen adsorption test at liquid nitrogen temperature. The results of these tests are summarized in this report.

Figures 5 and 6 show the adsorption isotherms obtained on samples from Calpine Co.'s well MLM-3 at different temperatures. Figure 5 was for granulas from core fragments with an average size of approximately 6mm equivalent diameter while Figure 6 was for the same core but smaller size (approx 1mm). As shown in the figures, the adsorption isotherms are affected by temperature. At low relative pressures, the effect of temperature on the amount of adsorption is negligible. However, the effect of temperature at higher relative pressure is apparent and consistent. The reason for the temperature effect on water adsorption isotherms is not clear and further investigation is required. Comparison of Figures 5 and 6 indicates that the size of the sample used has negligible effect on the adsorption isotherm.

Figure 6: Isotherms on Calpine Well MLM-3 Core B

Figure 7 shows an example of the adsorption/desorption isotherms on Calpine Co.'s well MLM-3 core. Significant hysteresis exists and persists to very low pressure, similar to those reported previously. The origin of the hysteresis is not clear to us and further investigation is needed.

As mentioned in the previous report (April-June, 1993), we plan to run systematic adsorption tests to evaluate the possible variation of the adsorbed quantity with rocks from different depths of the same well or from the same depth of different wells. However, such core samples or even core fragments are difficult to obtain. As an alternative, well cuttings are used. Our experiments show that the adsorption isotherms obtained on well cuttings are similar to those on core fragments. Although the amount adsorbed at the same temperature and pressure on well cuttings is slightly higher than that on the core fragment due to the presence of the fines in the air drilled cuttings, comparison of adsorption isotherms on well cuttings from different depths of a well should yield the type of information we need. We have 10 well cuttings from well Prati State 12, Northwest Geysers, available for adsorption tests. The measured depth (M.D.) of these samples together with the surface areas are summarized in Table 1. So far we have run water adsorption tests

Figure 7: Adsorption/Desorption Isotherms on Calpine Well MLM-3 Core B

on three of these samples. Figures 8 to 10 show the adsorption isotherms obtained at different temperatures.

Figure 11 shows a comparison of the isotherms on the three samples at 120°C . As shown in the figures, the amount of water adsorbed increases linearly with relative pressure up to about 0.7 for samples 2 and 4. For sample 1 the linear range is larger. This is probably due to the large surface area of this sample. Comparison of these adsorption isotherms with their corresponding surface area suggests that the amount of water retention on these well cuttings is proportional to their surface area for relative pressures up to 0.8.

The surface areas of the 10 well cuttings from Well Prati State 12 and a number of other rock fragments were measured using a surface area analyser, Gemini 2370 on loan from Micrometrics. The results are summarised in Tables 1 and 2. Examination of Table 1 reveals the heterogeneous nature of reservoir rocks. For a measured depth span of 4600 feet, the measured surface area varies from 0.7 to 3.2 and the variation appears to be random.

Water adsorption tests will be conducted on the remaining well cuttings from well Prati State 12 in order to get information on the variation of water

Figure 8: Adsorption Isotherms on Well PS12 Sample 1

Figure 9: Adsorption Isotherms on Well PS12 Sample 2

Figure 10: Adsorption Isotherms on Well PS12 Sample 4

Figure 11: Comparison of Adsorption Isotherms at 120°C

retention with the depth of the well. Further work will be conducted to understand the effect of temperature on water adsorption isotherms and the origin of adsorption/desorption hysteresis.

3 EFFECTS OF ADSORPTION ON REINJECTION AT THE GEYSERS

This research is under the direction of Research Assistant John Hornbrook and Professor Roland N. Horne.

This research is designed to answer fundamental questions about adsorption phenomena in geothermal reservoirs and to use these fundamentals to determine the effects of an adsorbed phase on tracer response at the Geysers geothermal reservoir. The research is broken into several sections, each of which is designed to answer questions about the adsorbed phase and its effects in geothermal reservoirs.

3.1 Thermodynamics of adsorbate

Thermodynamics of adsorbed and condensed phases are calculated by use of fundamental thermodynamic relationships. In particular, the density, internal energy and heat of adsorption/vaporization of the adsorbed and condensed phases are calculated and compared for a range of conditions. These data are necessary for accurate modeling of adsorbate effects. We have concluded:

1. Density and internal energy of the adsorbed phase and the capillary condensed phase are only slightly different from saturated water values at a given temperature. Thus, from a thermodynamic standpoint, there is no difference between adsorbate and capillary condensate.
2. Heat of vaporization/desorption for a retained liquid phase can vary from that for saturated water to a value about 30 percent greater for adsorbed liquid. The heat of vaporization/desorption depends upon the curvature of the liquid/vapor interface and the pore size distribution with the heat of desorption existing as an upper limit.

3.2 Heat effects of adsorbate

The assumption of thermal equilibrium in the presence of an adsorbed phase is tested. The effects of an adsorbed phase on heat transfer from the matrix to the liquid phase is analyzed. Based on results of fundamental heat transfer analyses, the entire heat balance for flow in geothermal reservoirs is studied to determine the effects of adsorption. Conclusions indicate that the heat balance is largely unaffected by the presence of an adsorbed phase and that, even at large adsorbate saturations, single phase vapor flow may be approximated as isothermal.

3.3 Numerical solution

An implicit pressure explicit saturation and temperature finite difference numerical scheme has been developed to model single phase vapor flow in the presence of a pressure dependent adsorbed phase. The effects of an adsorbed phase on pressure depletion were studied. Preliminary investigations were carried out on a simulated linear core. Figure 12 indicates that the pressure maintenance effects of an adsorbed phase can be large.

The numerical solution was also used to determine if the assumption of isothermal flow is valid for derivation of an analytical solution. Figure 13 indicates that the isothermal assumption is valid.

3.4 Analytical solution

An analytical solution for isothermal flow of vapor in the presence of an adsorbed phase is derived to isolate mass and mass rate of change effects of adsorbate on pressure response in geothermal reservoirs. The dimensionless form of the analytical problem is:

$$\frac{\partial^2 m}{\partial x^2} = [1 - A(m) + B(m)] \frac{\partial m}{\partial \tau} \quad (2)$$

where:

1. m = dimensionless psuedo-pressure.
2. x = dimensionless distance.

3. τ = dimensionless pseudo-time.
4. $A(m)$ = function expressing mass adsorbed at a given pressure.
5. $B(m)$ = function expressing the rate of change of mass adsorbed at a given pressure.

Comparison of analytical results with numerical results with no adsorption indicates that the analytical scheme is correct (Figure 14). However, suitable accuracy has yet to be attained for large adsorption saturations.

3.5 Tracer response

Production tracer histories from the Geysers geothermal reservoir are analyzed to determine the effects of the presence of several retardation mechanisms on the fate of injected fluids.

Figure 15 shows an early initial production spike of tracer followed by a long, low concentration production of tracer. This type of production is seen in several production wells at the Geysers and questions as to the cause of this production delay must be answered. Possible delay mechanisms include diffusion, adsorption, and partitioning. Preliminary conclusions indicate that none of the three delay mechanisms listed above are adequate by themselves to explain the delay of tracer production.

4 SIMULTANEOUS ANALYSIS OF TRACER AND WELL TEST DATA

This investigation is performed by Research Assistant, Xianfa Deng, and Prof. Roland N. Horne. The objective is to combine the analyses of tracer and well test data from geothermal reservoirs. So far in this project we have been working on the problem of pressure transient analysis of heterogeneous reservoirs. The current stage of the task is to begin the inclusion of tracer transport effects. The first requirement is to model the tracer problem for radial flow in homogeneous reservoir.

Denote the Peclet number by $P_e = \frac{vL}{\phi D}$ where v is the Darcy velocity, L is the length of the flow, ϕ is the porosity and D is the diffusion coefficient.

For two-component, one-phase linear flow, the solution has been obtained by solving the following convection-dispersion equation:

$$\frac{\partial C}{\partial t} + \frac{v}{\phi} \frac{\partial C}{\partial x} - D \frac{\partial^2 C}{\partial x^2} = 0. \quad (3)$$

For a radial system, the equation can be derived as

$$\frac{\partial C}{\partial t} + \frac{1}{r} \frac{\partial C}{\partial r} - \frac{1}{P_e} \frac{\partial^2 C}{\partial r^2} = 0. \quad (4)$$

Solutions to this equation are the focus of current activity in this project. The next steps will be to try interpreting tracer data and pressure data for the same reservoir. By investigating superposition for the convection-dispersion equation in radial flow, we will know if a radial model can be applied to multiwell systems, where tracer is injected at more than one well. So far, all the tracer analysis has used the linear model because the solution is available and simple. However the tracer flow in the reservoir actually is propagating in all directions and is more like the radial flow model.

Another aspect which needs to be addressed before combining tracer data and pressure data is whether the two kind data reflect the same properties of the reservoir such as permeability, porosity or compressibility. In other words, will these parameters control the behavior of tracer flowing?

For the mathematical solution to the tracer problem, the Green's function approach will be attempted as has been shown in previous reports. For the Green's function method for pressure transient analysis in heterogeneous reservoirs, we have just finished the study and presented a technical paper at the Annual SPE meeting in early October.

Table 1: Summary of BET Surface Area for PS12 Well Cuttings

Sample No.	Measured Depth (feet)	Surface Area (m^2/g)
1	4800-4900	3.2
2	5300-5400	2.0
3	5800-5900	1.4
4	6300-6400	1.1
5	6800-6900	1.3
6	7300-7400	1.6
7	7800-7900	0.7
8	8300-8400	1.0
9	8800-8900	1.1
10	9300-9400	0.9

Table 2: Summary of BET Surface Area

Sample ID	Surface Area m^2/g
Geysers NEGU-17	0.3
Coldwater Creek Core	1.4
Coldwater Creek Well Cuttings	1.7
Prati 29 ST1	0.27
Calpine Co.'s MLM-3	1.1
Montiverdi 1	0.8
Montiverdi 2	0.2
Montiverdi 2B	1.3
Montiverdi 5A	8.2
Montiverdi 7	1.4

Figure 12: Effect of adsorbed phase on pressure depletion

Figure 13: Effects of temperature decline on pressure history

Figure 14: Comparison of analytical and numerical solutions

Figure 15: Tracer production history at Geysers