PROCEEDINGS, Nineteenth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 18-20, 1994
SGP-TR-147

THE EFFECTS OF CO_2 ON STEAM ADSORPTION

Steve Palar and Roland N. Horne

Stanford University
Stanford, CA 94305

ABSTRACT

Water adsorption in geothermal reservoir materials was investigated by transient flow technique using steam and CO_2 gas. Theoretical and experimental results indicate that water adsorption exists in vapor-dominated type of reservoir, but experiments in the past have been limited to pure gases.

The common presence of CO_2, a non-condensible gas, in a geothermal reservoir necessitated a study of the effect of partial CO_2 concentration on adsorption. Experimental laboratory work using a crushed Geysers rock sample at low pressure was carried out. Transient pressure exerted by steam pressure inside the sample was measured against time during a desorption process. It was found that the partial presence of CO_2 did not significantly affect the adsorption of water.

INTRODUCTION

It is believed that vapor-dominated geothermal reservoirs (e.g. The Geysers) have liquid water in their pore space. The existence of the liquid water has been detected by using the following approaches :
- gravity & seismic method (Denlinger, 1979)
- material balance method (Ramey, 1990)

More steam production has been observed from The Geysers than be accounted for by means of superheated vapor thermodynamics. Due to the density difference between water and steam, large quantities of steam can be stored in a form of adsorption. The theory of adsorption provides a good explanation for the existence of the liquid water in this type of reservoir.

The presence of non-condensible gases is common in geothermal fields. The mole percentage of the non-condensible gases varies among reservoirs. It was reported that up to 80 % concentration of these gases was measured in Italy's Bagnore geothermal field. Total non-condensible gas in the Geysers varies from 4,000 to 80,000 ppm by weight (Haizlip and Truesdell, 1992).

CO_2 is by far the most common non-condensible gas found in a geothermal field. In The Geysers, Truesdell et al. (1992) reported that the measured concentration of this gas in ppm by weight ranged as follows :

Northwest Geysers	7,450 - 55,500
Central & Southwest G.	2,080 - 11,500
Southeast Geysers	94.70 - 734

In comparison, the geothermal fluids from New Zealand's Broadland field had 10 % of CO_2.

ADSORPTION OF WATER

The term adsorption used here refers to surface adsorption. There are two types of surface adsorption, physical and chemical. The main differences are that physical surface adsorption, also called physisorption, occurs at low temperature and has a lower heat of adsorption.

The presence of liquid water in a porous dry steam reservoir can be caused by capillarity and/or adsorption depending on the pore size. In his study on adsorption in porous media, Hsieh (1980) discounted the effect of capillarity, but not adsorption in micropores, which are pores with radii less than 20 Å.

Surface adsorption plays a major role in the retention of liquid water in micropores at pressures below the saturation pressure. Since the density of hot liquid is approximately ten times greater than that of steam vapor, up to ten times the mass of the steam can be stored as adsorbed water at elevated temperatures.

The adsorbed liquid water in a porous media creates a pressure lowering of the saturated vapor pressure at a particular temperature. This explains the presence of the two-phase water and steam, under conditions that would normally be superheated.

This adsorbed liquid water has different properties than non-adsorbed water. Economides, et. al. (1982) wrote that properties, such as density, compressibility and viscosity might be different for the two waters. Moreover, the molecules of adsorbed water are very compact.

Using kinetic theory, Langmuir (1916) investigated surface adsorption. His modified isotherm equation is :

$$X = \frac{\frac{P}{P_{sat}}}{A + B\frac{P}{P_{sat}}}$$

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. Terms A and B are constants and both determine the shape of the isotherm.

The limiting condition of this equation is that only one adsorption layer forms at each adsorption site. Intuitively this might not be true, however it has been found (Nghiem and Ramey, 1991) that this equation successfully matches the experimental data.

EFFECTS OF CO_2 ON ADSORPTION

CO_2 is characterized by its high saturation pressure. The presence of CO_2 in the binary mixture of CO_2 and water will elevate the saturation vapor pressure (dew point) of pure water at a temperature. The single saturation pressure line of pure water is replaced by bubble point and dew point curves for the mixture.

The amount of elevated pressure above the normal saturation vapor pressure for the pure water can be calculated if the composition of CO_2 and the temperature are known. The equilibrium constant K, which is the ratio of vapor phase to liquid phase, for the CO_2 and H_2O can be calculated accordingly (Sutton, 1976).

Solubility of CO_2 in the adsorbed water and non-adsorbed water is not the same (Economides, et al. 1982). The equilibrium constant K, for the adsorbed water is much larger than the non-adsorbed water. As a result, the solubility of CO_2 in the adsorbed water is much less. Economides et al. calculated the solubility of CO_2 in the non-adsorbed water and found that the mole fraction of CO_2 would range from 0.0005 to 0.001 in a typical geothermal reservoir. Thus the presence of CO_2, if any, is mainly in the pore space away from the adsorbed water.

EXPERIMENTAL WORK

Apparatus and Procedure

The equipment for this transient pressure experiment is on loan to Stanford Geothermal Program from USGS. The schematic diagram of the equipment is shown in Figure 5. It basically consists of 3 main systems :

- The Air Bath System
- The Vacuum System
- The Data Recording System

Pneumatic valves inside the enclosed air bath are controlled from the outside of the air bath. Also located outside the air bath are a vacuum pump and a data logger.

A sample was prepared beforehand by crushing and sieving it to a predetermined mesh size. The uniform and homogeneous sample was then placed in a 2-ft sample holder, located inside the air bath. Entrapped air inside the sample was subsequently evacuated by means of a vacuum pump for at least 24 hours.

The air-free sample then was ready to receive steam. The steam was generated inside the air bath. After an equilibrium was reached, the transient pressure experiment could be performed.

Two pressure transducers are located on ends of the sample holder. The experiment started when the bottom end of the sample holder was exposed to atmospheric pressure. The pressure change on top of the sample was recorded by the top transducer, connected to the data recording system. This transient pressure change over time is depicted in Figures 2 and 4.

The temperature in this experiment was maintained at about 125^0 C (257^0 F), which corresponds to a saturation steam pressure of 33.7 psia (steam table). This was the initial pressure of the steam inside the sample prior to the run.

The sample used was from Calpine Corporation's South Geysers well MLM-3, cored from a measured depth of 1325 m (1320 m TVD). The composition of this sample is mainly SiO_2 (67 %) and Al_2O_3 (12 %) by means of x-ray fluorescent test.

Two samples with mesh sizes of 20-45 and 45-150, and with measured permeability of 37.5 darcy and 0.207 darcy respectively, were subsequently used. The finer sample was extensively used due to its longer desorption time.

Experimental Result

The experiment is actually a desorption process, so the isotherms inferred are for desorption rather than adsorption.

Herkelrath, et al. (1983), experimenting with the transient flow of steam in porous media, observed a delay in the steam pressure breakthrough. The delay was attributed to adsorption. Their work ushered in a series of adsorption investigations by Luetkehans (1988), Harr (1991) and Qi (1993).

In order to compare the effects of sample size, the steam-only runs from the two different sample sizes are shown in Figure 1. Starting from the same initial pressure, the coarser-size sample did breakthrough earlier than the finer-size sample.

Interestingly both slopes of the semi-log graph are approximately 1 bar/cycle. The starting times for the decrease in pressure are 0.45 and 75 seconds respectively for the coarser and finer samples. It took 10 times longer than those times to reach its corresponding atmospheric pressure (Fig. 1).

Using a computer program developed by Qi (1993), it is possible to infer the shape and the parameters of the adsorption isotherm from the transient pressure data. The program utilized the 1-D finite-difference simulator developed by Nghiem and Ramey (1991) and modelled the isotherm profile based on the Langmuir equation. The inferred isotherms from the two experiments using the 20-45 Mesh size sample is shown in Figure 3. The isotherm of the 45-150 Mesh size sample is yet to be measured, pending the calculation of its porosity.

The shapes of the isotherms from the two experiments are both concave upward, however the values of the isotherm parameters A and B are very different. 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, among other things, by a discrepancy in the quantity of steam inside the sample prior to the desorption run.

Observations of the 100-% CO_2 runs for both samples show that when the initial CO_2 pressures are below the saturation steam pressure for that temperature, the shape of the corresponding curves do not display a steep decline and the pressure transmission is not delayed. Adsorption does not occur with CO_2. The steep pressure drop is only characterized by runs starting from the saturation steam pressure at that temperature.

Furthermore, it is observed that the transient pressure curves of steam-only and of mixture of steam and CO_2 do not show a noticeable difference. The partial presence of CO_2, up to a 36 % concentration, apparently did not affect the steam's pressure curve. This indicates that steam adsorption is unaffected by the presence of up to 36 % CO_2. Higher CO_2 concentration has not been tried yet.

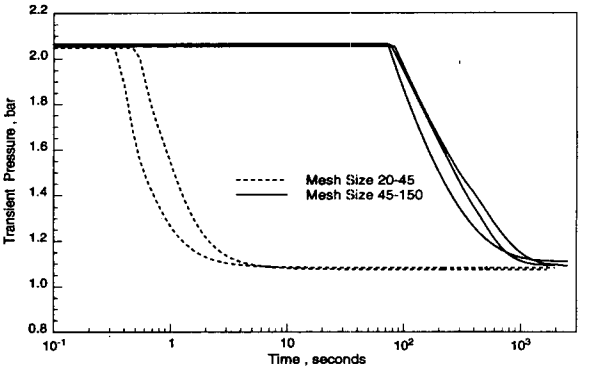

Figure 1: **Comparison of Mesh Size**

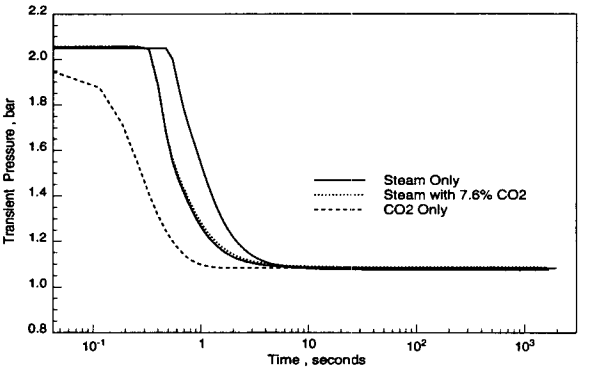

Figure 2: **Experiment with 20 - 45 Mesh Size**

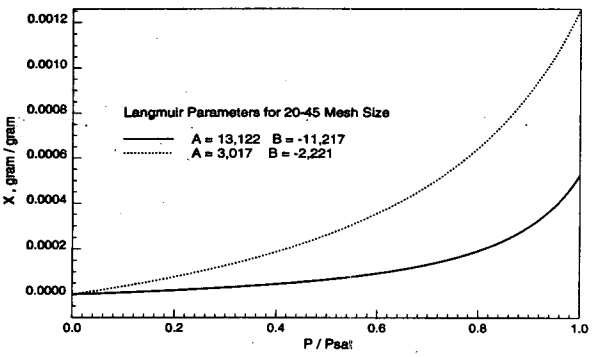

Figure 3: **Inferred Langmuir Isotherm**

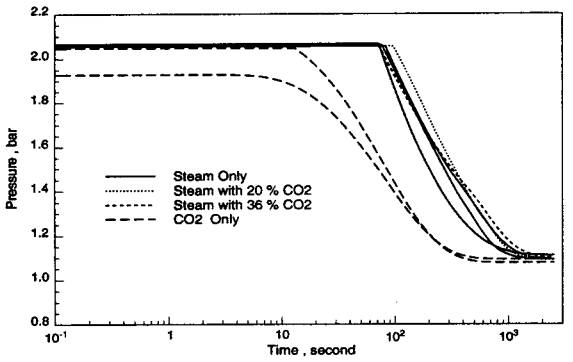

Figure 4: **Experiment with 45 - 120 Mesh Size**

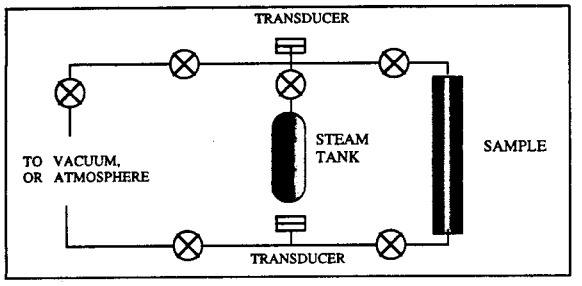

Figure 5: **Schematic Diagram of Apparatus**

CONCLUSION

Based on this laboratory work, it is apparent that the partial presence of CO_2 does not affect the adsorption of steam in the samples used.

This work by no means conclusively answers all the questions related to the effect of CO_2 on adsorption, however it presents a preliminary understanding of the effects.

ACKNOWLEDGMENTS

We thank the U.S. Department of Energy, Geothermal Division, for the support of this work, under Contract No. DE FG07 90 1D12934.

We also thank USGS, Calpine Corporation and UURI (University of Utah Research Institute) for making this work possible.

REFERENCES

1. Denlinger, R.P.: "Geophysical Constraints on The Geysers Geothermal Field, Northern California", Ph.D. Thesis, Stanford University, (1979).

2. Ramey, H.J., Jr.: "Adsorption in Vapor-Dominated Systems", Proc. Eighth Geothermal Program Review, San Francisco, 63-67, (1990).

3. Haizlip, J.R., and Truesdell, A.H.: "Noncondensible Gas and Chloride Are Correlated in Steam at The Geysers", Monograph on The Geysers Geothermal Field, Geothermal Resources Council's Special Report No. 17, 139-143 (1992).

4. Truesdell, A.H., Box, W.T., Jr., Haizlip, J.R., and D'Amore, F.: "A Geochemichal Overview of The Geysers Geothermal Reservoir", Monograph on The Geysers Geothermal Field, Geothermal Resources Council's Special Report No. 17, 121-132 (1992).

5. Hsieh, C.H.: "Vapor Pressure Lowering in Porous Media ", Ph.D. Thesis, Stanford University, (1980).

6. Economides, M., Ostermann, R., and Miller, F.G.: " Implications of Adsorption and Formation Fluid Composition on Geothermal Reservoir Evaluation", Proc. International Conference on Geothermal Energy, Florence, Italy, Vol. 1, 149-162 (1982).

7. Nghiem, C.P. and Ramey, H.J., Jr.: "One-Dimensional Steam Flow in Porous Media", *Stanford Geothermal Program Report*, No. SGP-TR-132, (1991).

8. Langmuir, I.: "The Constitution and Fundamental Properties of Solids and Liquids, Part I. Solids", *J. Amer. Chem. Soc.*, Vol. 38, 2221-2295, (1916).

9. Sutton, F.M.: "Pressure-Temperature Curves for a Two-Phase Mixture of Carbon Dioxide and Water", *New Zealand J. of Sc.*, Vol. 19, 297-301, (1976).

10. Herkelrath, W.N., Moench, A.F., and O'Neal II, C.F.: " Laboratory Investigation of Steam Flow in a Porous Medium", *Water Resources Research*, Vol. 19, No. 4, 931-937 (1983).

11. Luetkehans, J.: "A Laboratory Investigation of Steam Adsorption in Geothermal Reservoir Rocks", Master's Thesis, Stanford University, March, (1988).

12. Harr, M.S.: "Laboratory Measurement of Sorption in Porous Media", Master's Thesis, Stanford University, August, (1991).

13. Qi, M.: "Estimation of Adsorption Parameters from Experimental Data", Master's Thesis, Stanford University, May, (1993).