NOTICE CONCERNING COPYRIGHT RESTRICTIONS

Measurement of Surface Area and Water Adsorption Capacity of Geothermal Reservoir Rocks

S. Shang, R. N. Horne, and H. J. Ramey, Jr.
Petroleum Engineering Department
Stanford University, CA 94305-2220

Abstract

The measurement of the quantity of adsorbed water on geothermal reservoir rocks allows a more realistic estimation of reserves for vapor–dominated geothermal reservoirs. This study measured adsorption/desorption isotherms of water vapor on Geysers rock samples from Calpine Co.'s well MLM-3, both core fragments and well cuttings from Coldwater Creek steamfield, a number of well cuttings from well Prati State 12, Northwest Geysers steam field, and well cuttings from Montiverdi, Italy. Surface areas of these rock samples were measured using nitrogen adsorption at 77K. The results of these measurements suggest that surface area is a crucial factor in determining the amount of water adsorption. Analysis of the water adsorption data indicates that adsorption is the dominant phenomenon in the matrix of the reservoir rock at relative pressures below 0.8. Depending on the structure of the rock, capillary condensation contributes considerably to the total water retention at relative pressure between 0.8 and 1.0. However, there is no clear distinction between adsorption and capillary condensation and it is difficult in the experiments to determine when complete saturation occurs.

A significant result of these experiments was the demonstration that well cuttings show adsorption characteristics very much like those obtained from core fragments. This should allow further adsorption measurements to be made more extensively and at lower cost.

Introduction

Adsorption of water onto vapor dominated geothermal reservoir rocks, and the adsorbed water as a possible storage mechanism for these reservoirs have been topics of much discussion for the last few years (Ramey, 1990). However, water adsorption data on reservoir rocks, particularly at high temperature, are still scarce. Furthermore, there has been no systematic study to evaluate the possible variation of the adsorbed quantity with rocks from different parts of a reservoir. Available experimental data in our laboratory show that the amount of water adsorbed varies depending on the types of rock studied (Shang et al., 1993, 1994). This indicates that the adsorbed quantity on rocks from different depths of a well may change since the structure as well as the lithology of the rock vary with location. Such information is important in terms of both understanding the reservoir production behavior and aiding the design of reinjection processes.

This paper presents results of our continuing effort on water adsorption research. Included in the paper are water adsorption isotherm measurements on rock samples from Calpine Corporation well MLM-3, South Geysers field, both core fragments and well cuttings from well Prati State 12, Northwest Geysers field and Montiverdi, Italy. Surface areas of these samples were also measured.

Multilayer Adsorption Isotherms

The general characteristics of physical adsorption and the commonly used adsorption isotherms were reviewed previously (Shang, et al., 1994). The following is a brief summary of the Brunauer, Emmett and Teller (BET) isotherm, and the Frankel–Halsey–Hill (FHH) isotherm. These two isotherm equations are used to analyse the measured adsorption data in this study.

BET Isotherm

The BET isotherm was developed to account for multilayer adsorption (Brunauer, et al., 1938), and it has the following form.

$$\frac{q}{q_m} = \frac{b(p/p^o)}{(1 - p/p^o)(1 - p/p^o + bp/p^o)} \tag{1}$$

where q is the amount adsorbed, q_m is the amount adsorbed at monolayer coverage, p is pressure, p^o represents the saturation vapor pressure of the adsorbate at the relevant temperature, and b is a constant. This isotherm has been widely used to determine the surface area of an adsorbent from experimental data in the relative pressure range of $0.05 < p/p^o < 0.3$. However, the best fitting BET equation normally predicts too little adsorption at low pressures and too much adsorption at high pressures (Adamson, 1990). The BET isotherm was only used to extract surface area from nitrogen adsorption data.

FHH isotherm

The FHH (Halsey, 1952) equation was developed based on an assumed variation of adsorption potential with distance from the surface, and generally fits multilayer adsorption data over a wide relative pressure range (Adamson, 1990). The isotherm equation is written as follows,

$$\left(\frac{q}{q_m}\right)^n = \frac{A}{ln(p^o/p)}; \qquad A = \frac{\epsilon_o}{x_m^n RT} \tag{2}$$

where x_m is the film thickness at the monolayer coverage, n and A are empirical parameters, and ϵ_o is the potential of the solid surface for adsorption. The above equation is further simplified into a two parameters correlation for the purpose of fitting adsorption isotherm as follows,

$$q^n = \frac{B}{ln(\frac{p^o}{p})} \qquad (3)$$

where B is a lumped parameter containing information about the capacity of the surface for adsorption. The FHH isotherm is attractive for its simple mathematical form, and was used to fit water adsorption isotherms in this study.

Adsorption and Saturation

In dealing with reservoir engineering problems, saturation is a parameter of great concern. The amount of water adsorbed at any given temperature and pressure can be converted to saturation according to the following equation,

$$S_w = \frac{1 - \phi}{\phi} \frac{\rho_r}{\rho_w} q \qquad (4)$$

where ϕ is the porosity of the rock, ρ_r and ρ_w are the densities of the rock and the adsorbed phase, respectively.

Apparatus and Procedures

PMI Sorptomer

A schematic of the sorptometer used in this study is shown in Figure 1. It consists of three parts: (1) a set of valves and pressure transducers kept in a high-temperature chamber to avoid water condensation, (2) a sample chamber for loading and unloading the samples, and (3) the electronics for automatic control. The sample chamber has a separate heating system so that the samples can be heated at temperatures higher than the test temperature. During normal operation, one only needs to load the sample and the rest of the procedures are accomplished under computer control.

The principle of the water adsorption/desorption measurement is the same as a BET type experiment. The quantities measured are the pressures of water vapor in the system before and after adsorption/desorption. The first step in the measurement is to evacuate the sample till a desired vacuum is obtained. Then valves V1, V2 and V4 are closed. Opening V9 will introduce steam into the system. Pressures gauge P measures the pressure in the system (Valve Vv will open automatically to use Pv when the pressure is below 10 Torr). When a desired pressure (initial pressure) is reached, Valve V9 will close, and valves V1 and V2 will open. System pressure will change due to the adsorption of water onto the adsorbent sample. When it reaches a stable value, the pressure reading is taken as an equilibrium value (final pressure). Knowing the initial and final pressures and the volumes of the system, we can calculate the quantity adsorbed from mass balance. This produces one point on the adsorption isotherm. The procedures are repeated till a complete isotherm is obtained. Desorption commences at the end of the adsorption test. In this case, water vapor is gradually pumped away until the adsorbed water is completely desorbed. The needle valves are used to avoid abrupt changes in pressure. Nitrogen is used for system calibration.
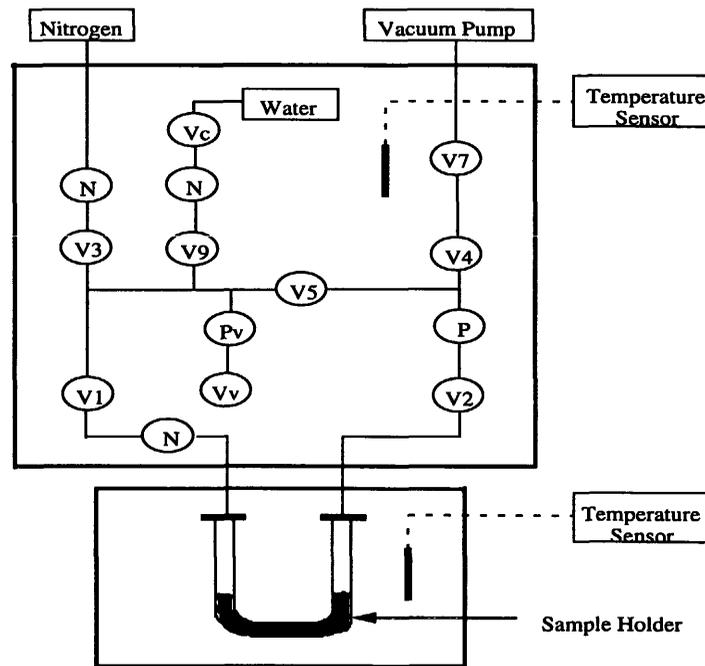
Key: N for needle valves   V for solenoid valves
       P for pressure gauge   Pv for vacuum gauge

Figure 1: A Schematic of the PMI Sorptometer

Due to the limitation of the sample holder size, rock samples had to be broken into granulars with equivalent diameters less than 8 mm. This should not impose any problem since the only change caused by breaking the core is surface area and the change is likely to be small. It was found to have negligible effect on the amount of water adsorbed (Harr, 1991). On the other hand, using small size samples reduces diffusional time and the time required for adsorption/desorption equilibrium. New samples were all heated at $180^\circ C$ under vacuum overnight to get rid of any surface residuals before running the adsorption test. Knowing the complexity of the adsorption process, it is important to ensure that the rock surface has the same condition prior to each adsorption test. This was achieved by heating the sample under vacuum at a temperature $50^\circ C$ higher than the test temperature for 2 to 4 hours. Reproducible isotherms were obtained after this pretreatment.

The PMI sorptometer failed for nitrogen adsorption test for two reasons. First of all, the maximum amount of sample that can be used for the test is small (ca. 20 grams) due to the size of the sample holder and chamber. Secondly, it was difficult to maintain a constant liquid nitrogen level. Both factors are important since reservoir rocks typically have small surface area.

Surface Area Analyzer

The surface area of the rock samples were measured using nitrogen adsorption at $77K$. The measurements were carried out using a surface area analyzer, Gemini 2370, on loan from Micromeritics. The Gemini 2370 uses a flow–gas technique in which nitrogen flows into both the sample and the balance tubes at the same time. The only difference between the two tubes is the presence of the sample in one of them. The delivery rate of nitrogen into the sample tube is controlled by the rate at which the sample can adsorb nitrogen onto the surface. The rate of flow into the balance tube is controlled to give the same pressure. The quantity adsorbed at a given pressure is measured by pressure difference in the two vessels connected to the two tubes. The BET equation was used to fit the adsorption data to obtain the desired surface area.

Results and Discussion

Tests on MLM-3 Rock

Figure 2 shows an example of the adsorption/desorption isotherms on Calpine Co's well MLM-3 rock obtained at $120^\circ C$. For engineering convenience, the amount of water adsorbed was converted into saturations using Eqn. 4. A rock density of 2.7 g/cm^3 and bulk water density of 0.943 g/cm^3 was used. The major uncertainty is porosity which is difficult to measure for low porosity rocks. A porosity of 2% was used in the calculation. Significant hysteresis exists and persists to very low pressure. The possible causes for the observed hysteresis are structural heterogenity of the rock, capillary condensation and chemical interaction of water molecules with rock surface as explained previously (Shang et al., 1994).

The simplified FHH equation, Eqn. 3, was used to fit the adsorption isotherm shown above. Figure 3 shows the measured and fitted isotherms for Calpine Co's well MLM-3 rock. With fitted parameter values of 0.76 for B and 1.4 for n, the FHH equation fits the adsorption isotherm reasonably well.
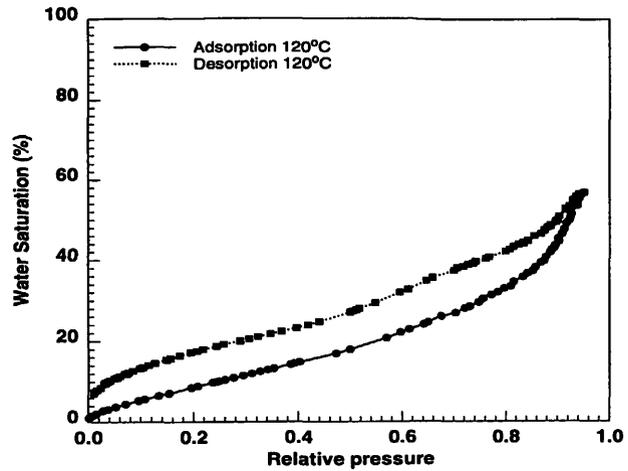
Figure 2: Isotherms for MLM-3 Sample
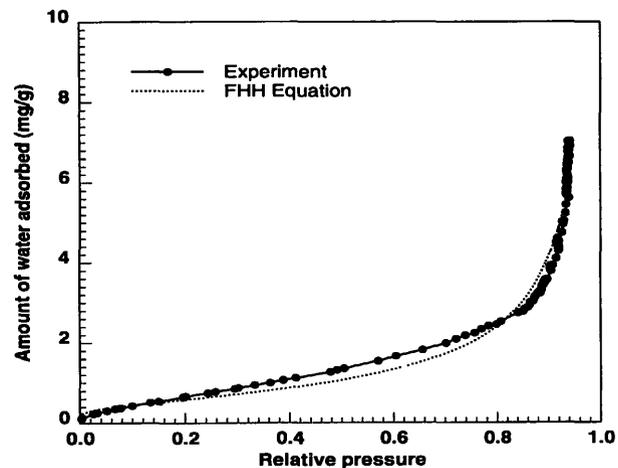
Figure 3: Measured and Fitted Isotherms
on MLM-3 Sample

The effect of temperature on water adsorption has been shown to be sample dependent (Hsieh, 1980, Herkelrath et al., 1983). Water adsorption tests were carried out on well MLM-3 rock at temperatures from 90 to $130^\circ C$ and Figure 4 shows the results of these tests. At low relative pressure, changes in the amount of water adsorbed with temperature is small. As relative pressure increases, the effect of temperature on water adsorption becomes more appreciable. Chemical interaction of water molecules with rock surface and its subsequent enhancement on water retention is one of the possible reasons for the observed temperature effect. The effect of temperature on water retention requires further study.

Comparison on Core and Well Cuttings

Reservoir rock samples in the form of core or core fragments are not readily available in specified locations. However, well cuttings are. In order to decide whether water adsorption on well cuttings represents that on the core, tests were performed on both core fragments and well cuttings of the same
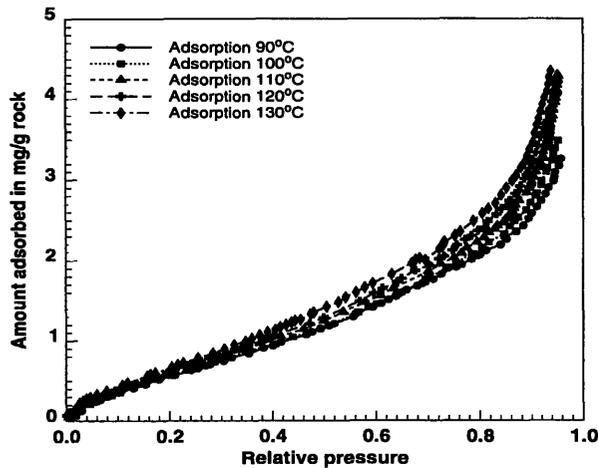
Figure 4: Adsorption Isotherms on MLM–3 Sample
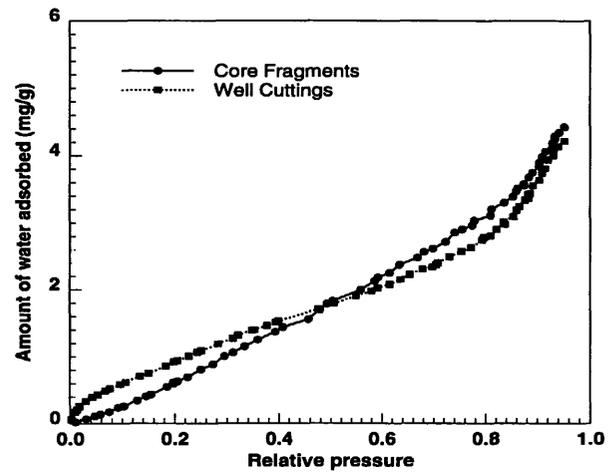
Figure 5: Adsorption Isotherms on Core and Well Cuttings

well location from the Coldwater Creek steamfield. Initial tests showed substantially more adsorption on the well cuttings than that on the core fragments. It was found that the presence of some foreign material (tentatively identified as clays from the drilling process) was the source of contribution to the higher adsorption on the well cuttings. Due to its distinguishing color, these foreign particles were easily removed. Figure 5 shows a comparison of the two adsorption isotherms obtained at 120°C. Considering experimental error, the agreement between the two data sets is acceptable. Thus, we concluded that it will be acceptable to use well cuttings from different parts of the Geysers for systematic water adsorption tests.

Measurement of Surface Area

It has been shown that the amount of adsorption depends on the type of geologic media and that the surface area of the media is a crucial factor in determining the quantity adsorbed (Shang et al., 1994). It is, therefore, important to measure the surface area of the rock samples used for water adsorption tests. Such measurements were carried out using the Gemini 2370 surface area analyser described previously. The results for 10 well cuttings samples from well Prati State 12, Northwest Geysers, and other samples discussed earlier are summarised in Table 1. Examination of Table 1 shows that for a depth span of 4600 feet, the measured surface area varies from 0.7 to 3.2 m^2/g and the variation appears to be random. This clearly reveals the heterogeneous nature of reservoir rocks.

Adsorption Capacity and Surface Area

Figure 6 shows a comparison of water adsorption isotherms obtained on seven Prati State 12 well cuttings at 120°C. The depth and the measured surface area of these samples are shown in Table 1. For all the samples studied, adsorption dominates the process of water retention for relative pressures up to about 0.8. As pressure is further increased, capillary condensation becomes more important. At a given pressure, the amount of water adsorbed varied considerably among the seven samples. The variation appears to be random with respect to depth. However, it does depend on the surface area of the samples. Knowing the
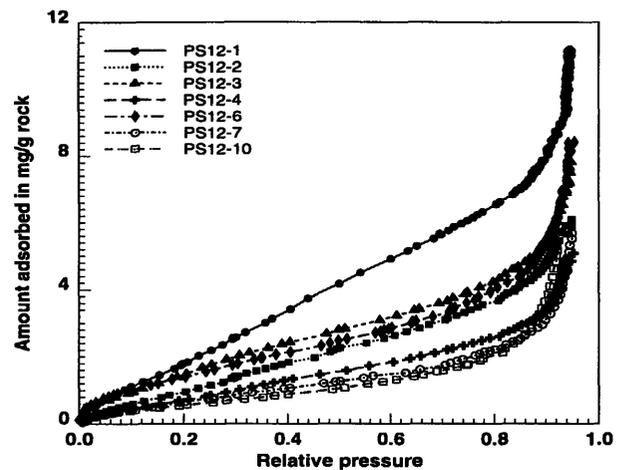
Figure 6: Adsorption Isotherms on PS12 Well Cuttings

surface area of the samples, we can express the amount adsorbed as weight per unit surface. Figure 7 shows the comparison of the isotherms on the basis of unit surface. If physical adsorption is the only process occuring, the isotherms should fall onto the same curve. This is not the case, however, particularly at high relative pressures when capillary condensation contributes substantially to the total water retention. This supports our previous conclusion that the surface area of a rock sample is a primary factor in determining its water adsorption capacity and capillary condensation is a dominant process in water retention at high relative pressures.

A second set of tests was performed on well cuttings samples from Montiverdi wells. Figure 8 shows a comparison of the adsorption isotherms measured at 120°C. Clearly, the sample from Montiverdi 5 exhibits a much higher adsorption capacity compared to other samples. This is expected since the sample from Montiverdi 5 possess an unusually high surface area for reservoir rocks. Comparison of the isotherms based on unit surface area is shown in Figure 9.

Table 1: Summary of the Measured Surface Area

Sample ID	Measured Depth (feet)	Surface Area (m^2/g)
PS12–1	4800–4900	3.2
PS12–2	5300–5400	2.0
PS12–3	5800–5900	1.4
PS12–4	6300–6400	1.1
PS12–5	6800–6900	1.3
PS12–6	7300–7400	1.6
PS12–7	7800–7900	0.7
PS12–8	8300–8400	1.0
PS12–9	8800–8900	1.1
PS12–10	9300–9400	0.9
Coldwater Creek Core	6260	1.4
Coldwater Creek Well Cuttings	6260	1.7
Calpine Co.'s MLM3	4330	1.1
Montiverdi 1	6429	0.8
Montiverdi 2B	9440	1.3
Montiverdi 5A	9512	8.2
Montiverdi 7	9706	1.4
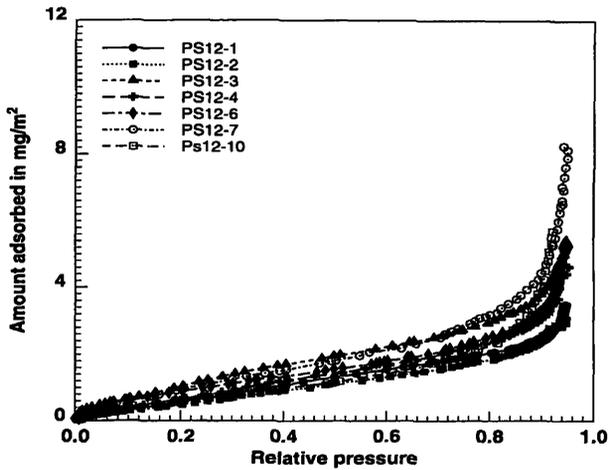
Figure 7: Adsorption Isotherms based on Surface Area
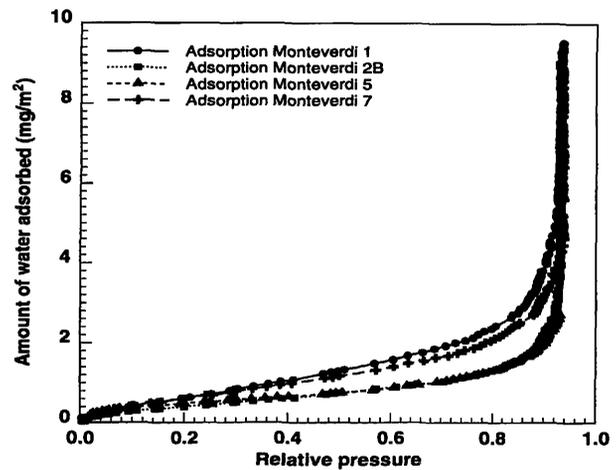
Figure 9: Adsorption Isotherms based on Surface Area
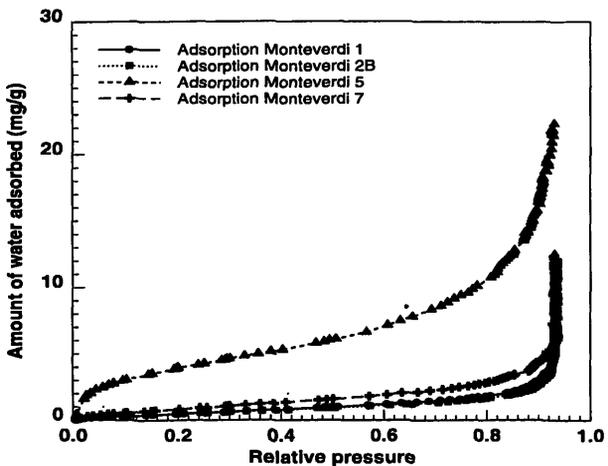
Figure 8: Adsorption Isotherms on Montiverdi Well Cuttings

Conclusions

Water adsorption/desorption hysteresis exists on the geothermal rock samples investigated. While rock heterogenity and capillary condensation are the commonly recognized source of hysteresis, chemical interaction also contributes to the hysteresis particularly at low pressures. The amount of water adsorption at a given relative pressure increases with increasing temperature for the samples studied.

Well cuttings can be used as substitutes for core samples for water adsorption studies. The amount of water adsorption depends on the type of geologic media and surface area is a crucial factor in determining the quantity adsorbed. Adsorption isotherms on different samples compare well for relative pressures below 0.8 when the comparison is based on unit surface area. The deviation at high relative pressures is due to the presence of capillary condensation. It is, thus, logical to suggest that surface area and porosity comprise the essential parameters in determining the capacity of a reservoir rock for water retention.

Shang, Horne, and Ramey Jr.

Acknowledgments

References

Adamson, A.W. (1990) *Physical Chemistry of Surfaces*, Wiley.

Brunauer, S., Emmett, P.H. and Teller, E. (1938) Adsorption of Gases in Multimolecular Layers. *J. Am. Chem. Soc.* **60**, pp. 309–319.

Halsey, G.D., Jr. (1952) On Multilayer Adsorption. *J. Am. Chem. Soc.* **74**, pp. 1082–1083.

Herkelrath, W.N., Moench, A.F. and O'Neal II, C.F. (1983) Laboratory Investigation of Steam Flow in a Porous Medium *Water Resource Research*, **19**(4), pp. 931–937.

Hsieh, Chih Hang (1980) *Vapor Pressure Lowering in Porous Media*, PhD Thesis, Stanford University.

Hsieh, Chih–Hang and Ramey, H.J., Jr. (1983) Vapor–Pressure Lowering in Geothermal Systems. *SPEJ*, **23**(1), pp. 157–167.

Harr, M.S. (1991) *Laboratory Measurement of Sorption in Porous Media*, Master' dissertation, Stanford University.

Ramey, H.J., Jr. (1990) Adsorption in Vapor–Dominated Systems. *Geothermal Program Review VIII*, San Francisco, CA.

Shang, S.B., Horne, R.N. and Ramey, H.J., Experimental Study of Water Adsorption on Geysers Reservoir Rocks, *18th Workshop Geothermal Reservoir Engineering*, January 1993, Stanford.

Shang, S.B., Horne, R.N. and Ramey, H.J., Study of Water Adsorption on Geothermal Reservoir Rocks, submitted to *Geothermics*, 1994.