# IMPROVING MODELS OF VAPOR-DOMINATED GEOTHERMAL FIELDS: THE EFFECTS OF ADSORPTION

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## Summary

Adsorbed water on the rock surfaces in vapor-dominated geothermal fields has long been thought to provide a major source of fluid within the reservoir. Over the past several years, the Stanford Geothermal Program has conducted a series of investigations into the phenomena of water adsorption in geothermal systems, and their effects on reservoir performance. The results and conclusions of the most recent studies will be summarized in this paper.

The studies include: (1) an experimental investigation in which measurements of the adsorption and desorption isotherms on actual geothermal cores were made, including a study of adsorption characteristics in The Geysers field in California; (2) a theoretical investigation into how adsorption relates to capillary condensation, and how the combined phenomenon can be expected to act; (3) a theoretical, numerical and data investigation into how adsorption and desorption will affect reinjection at The Geysers field, including a study of adsorption effects evident in tritium tracer observations.

It has been found through these studies that the amount of (liquid) water adsorbed in vapor-dominated geothermal fields is very considerable, even at pressures well below the boiling point pressure. Adsorbed water represents the major fraction of fluid stored in the reservoir and can be the most important source. Reservoir performance forecasts are strongly governed by the amount, and the rate of release of adsorbed water. Adsorption seems only modestly affected by the presence of noncondensible gases. During reinjection, water adsorbs more easily than it subsequently is able to desorb, which results in a reduction in the efficacy of reinjection.

## Introduction

In simple terms, a vapor-dominated geothermal reservoir consists of porous or fractured rock, with the interstitial spaces filled with steam. However, a more complete understanding of the behavior of this type of reservoir requires a more sophisticated description than this. Due to the processes of adsorption and capillary condensation, water molecules are stored on the surfaces of the pore spaces in a state that is more like that of a liquid than that of a vapor. This is true even if the thermodynamic conditions are such that liquid water could not exist in a free space. The consequence of the adsorption phenomenon is that water exists in the pore space of a vapor-dominated geothermal reservoir, even though the steam present in large fractures and voids may be superheated. The large surface area of a porous material and the large density difference between the liquid and vapor states of water mean that the mass of liquid constitutes the major component of fluid storage, even though it is only vapor that flows to the wells.

The performance of a vapor-dominated geothermal reservoir is governed strongly by the effects of adsorption. The liquid phase represents most of the fluid in the reservoir, and sustains production beyond what might be expected for a reservoir filled only with vapor. While this is a very beneficial effect, adsorption complicates the analysis of the reservoir since the liquid water is "invisible" to, the reservoir engineer. The useful life and sustainable production capacity of the reservoir is dependent on the quantity of adsorbed water in place, yet this quantity can be measured only indirectly. Furthermore, the effectiveness of reinjection into a vapor-dominated reservoir is also governed by the influence of adsorption. Hence, proper design and implementation of a reinjection scheme must take proper account of the adsorption phenomena.

Over the past several years, the Stanford Geothermal Program has conducted a number of investigations into the properties of adsorption and its effect on geothermal production and injection. The results of these studies will be summarized in the following sections. Separate issues to be discussed are: (1) What is adsorption? (2) How much adsorption occurs in geothermal reservoirs? (3) What are the properties of adsorbed water in geothermal rocks? (4) How does adsorption affect production and injection?

## What is Adsorption?

Physical adsorption is caused mainly by Van der Waals attractive forces, including the dispersion force. In addition, there will be electrostatic forces if either the adsorbent or the adsorbate is polar in nature. The process is similar to condensation of vapor molecules onto a liquid phase of the same composition. The major characteristics of physical adsorption can be summarized as follows (Satterfield, 1980; Ruthven, 1984):

1. Physical adsorption is an exothermic process so the amount of gas physically adsorbed at constant pressure always decreases monotonically as temperature is increased. The average heat of physical adsorption for the formation of a monolayer usually exceeds that of liquefaction, but seldom by more than a factor of about two.

2. Physical adsorption requires no activation energy and therefore can occur nearly as fast as molecules strike a surface. The process is reversible and equilibrium is established very rapidly unless diffusion through a fine porous structure limits the process.

3. Adsorption/desorption hysteresis is caused by geometric effects in that the specific curvature in contact with the vapor at a specified relative pressure ($p/p_0$) as vapor pressure is increased is different from that as the vapor pressure is decreased.

In a porous material, adsorption and capillary condensation are two closely related processes, i.e. they both cause the vapor to condense onto the solid. They are related in such a way that adsorption provides a precursor for capillary condensation. The physical processes of adsorption in porous materials can be divided into three steps: (1) submonolayer adsorption, (2) multilayer adsorption with transition to (3) capillary condensation. The pressure range at which the transition from multilayer adsorption to capillary condensation occurs depends on the structure of the material. If the material is microporous, the pore space will be filled up (commonly termed as volume filling) before multilayer adsorption is developed. In larger pores, multilayers of adsorbed water form as pressure increases. At a certain pressure, capillary condensation commences in the small pores. As the pressure is progressively increased, wider and wider pores are filled while multilayer adsorption is simultaneously taking place.

## Adsorption in Geothermal Reservoirs

In vapor-dominated geothermal systems, it has been proposed that liquid might exist as adsorbed liquid in micropores (White, 1973). Evidence from both laboratory studies (Hsieh, 1980, Herkelrath et al., 1983) and field data indicates that storage of liquid as micropore fluid is likely (Ramey, 1990). If it is assumed that the only mechanism for liquid storage is adsorbed water, then the desorption curve provides important information for performance matching and production forecasting. It is obvious that measurement of adsorptioddesorption of water vapor on reservoir rocks is a crucial step in determining whether adsorption is the storage mechanism for these systems, and if so, what would be the appropriate procedure for performance prediction of vapor dominated geothermal systems.

Reservoir related water adsorption studies have been limited, especially at high temperatures. Hsieh (1980) constructed a BET (Brunauer, Emmett, and Teller) type of apparatus for high-temperature adsorption measurements. Hsieh (1980) conducted a number of adsorption measurements on Berea sandstone and unconsolidated silica sand. It was concluded that the characteristic adsorption curves for consolidated cores are temperature invariant and that adsorbed water may be an important source of steam in vapor-dominated geothermal reservoirs (Hsieh and Ramey, 1983). Luetkehans (1988) continued Hsieh's work by improving the apparatus. Measurements of water adsorption isotherms were made on Berea sandstone, cores from The Geysers, California, and from Larderello, Italy. However, the true magnitude of the amount adsorbed was in question due to difficulties in establishing equilibrium. In addition, the long equilibrium time required made the leakage of high-temperature valves a significant factor in causing experimental error. Laboratory studies of water adsorption in porous media were also conducted by Herkelrath and his coworkers in association with their work on steam flow in porous media (Herkelrath et al., 1983) and the disposal of nuclear waste (Herkelrath and O'Neal, 1985). They reported a higher level of adsorption, but otherwise findings similar to those of Hsieh and Ramey (1983).

Clearly, there was a need to improve on the apparatus for water adsorption tests on geothermal rocks at high temperatures. It was appealing to automate the adsorption experiments in the interest of both sparing the operator for other tasks and in reducing experimental error. Harr (1991) performed preliminary investigations on the use of an automated sorptometer from Porous Materials, Inc. (PMI) for high-temperature water adsorption measurements. To our knowledge, this is the first commercial sorptometer built for automated high-temperature adsorption tests. The results of this series of measurements has been described in Shang, Horne and Ramey (1994a, 1994b) and will be summarized here.

Adsorption of water vapor on Berea sandstone and The Geysers well NEGU-17 graywacke was carried out at temperatures of 80, 100, 120 and 130°C. Fig. 1 shows the adsorptioddesorption isotherms on the two samples at 120°C. A comparison of this figure with similar measurements for Berea sandstone shows that the amount of water adsorbed at any given relative pressure is higher on Berea sandstone than on The Geysers graywacke. This is expected since Berea sandstone has a larger surface area. At relative pressures below 0.6, the amount of water adsorbed can be approximated by a linear function of relative pressure in both cases. However, the linear relationship breaks down as pressure increases and the amount of water adsorbed increases rapidly with pressure.

This change in the shape of the adsorption isotherm is an indication that capillary condensation has taken place and its contribution to total water retention by the reservoir rock becomes increasingly more significant as pressure is further increased.

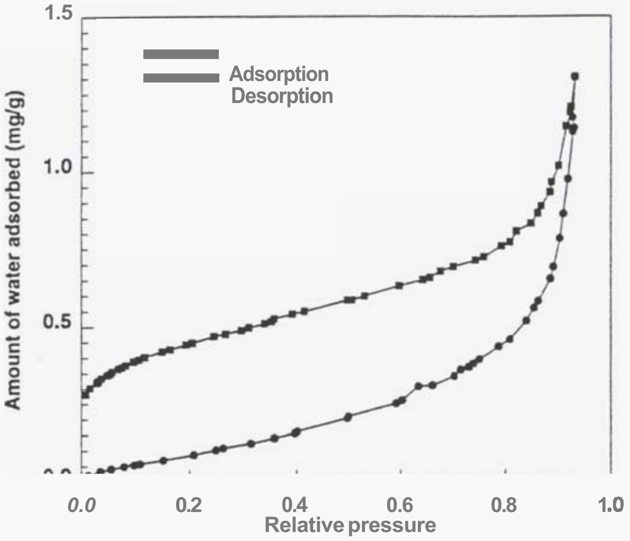


Figure 1: Water Adsorption/Desorption Isotherms for Geysers NEGU-17 Graywacke at 120°C

There is an obvious hysteresis and it persists to very low pressure. Detailed discussion on the occurrence and possible causes of the observed hysteresis for water adsorptioddesorption is presented in Shang, Home and Ramey (1994a).

Fig. 2 shows the variation of adsorption with temperature in a core from The Geysers. Comparison of Figs. 1 and 2 reveals that the overall quantity adsorbed varies from one part of the field to another. The same observation was made comparing measurements from reservoir samples from Italy.

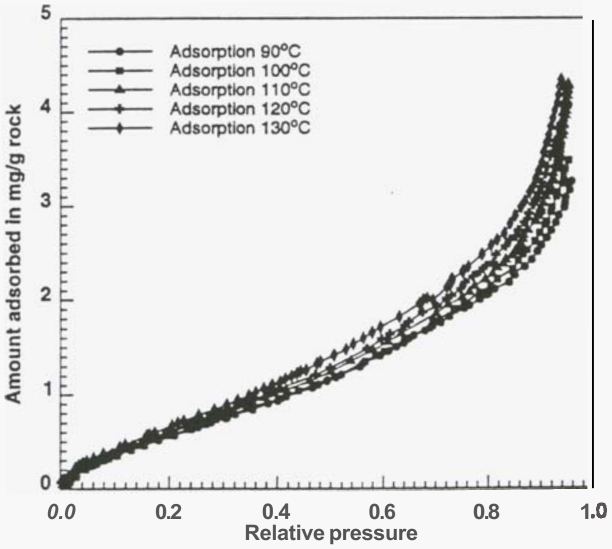


Figure 2: Adsorption Isotherms on Geysers MLM-3 Sample at Different Temperatures

Adsorption isotherms, such as those shown in Figs. 1 and 2, are often shown as mass adsorbed per mass of rock. It is useful to look at the mass adsorbed in terms of liquid saturation, by converting the mass adsorbed per mass of rock ($X$) using the following equation:

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

Making the conversion to water saturation reveals that adsorption accounts for a large volume of liquid water, as shown in Fig. 3 (which is a conversion of one of the isotherms from Fig. 2).

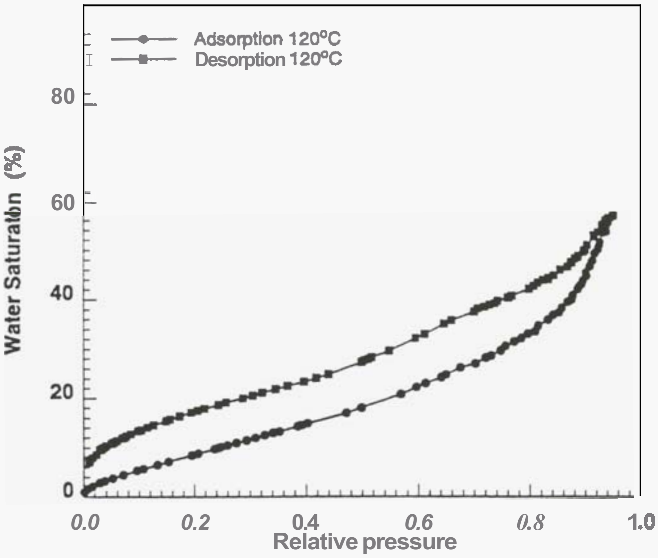


Figure 3: Adsorption Isotherms for Geysers MLM-3 Sample, Plotted as Saturation.

Based on these measurements, it can be concluded that a major fraction of the pore space in a vapor-dominated geothermal reservoir is filled with liquid water, even at pressure significantly below the saturation pressure.

An important result from Shang, Home and Ramey (1994a) was that measurements of adsorption made using cores were effectively the same as those made using cuttings from the same well. Since cores are usually difficult and expensive to obtain, this means that adsorption measurements can be made over a wide range of reservoir locations. Fig. 4 shows a comparison of adsorption measurements made on cuttings from a Geysers well, compared to measurements made on a core from the same well.

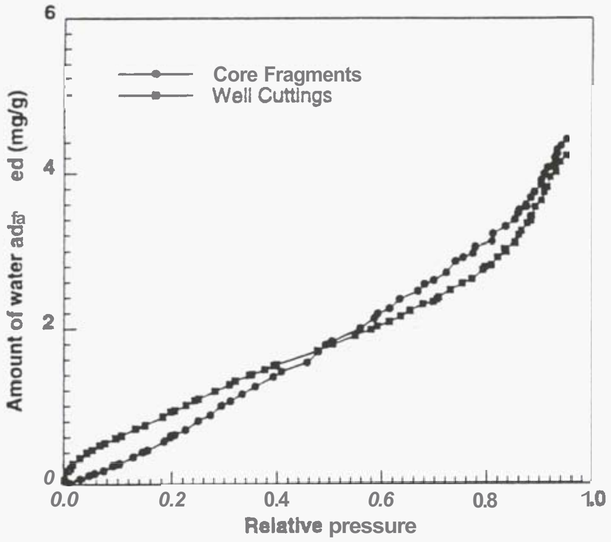


Figure 4: Comparison of Adsorption Isotherms on Core and Well Cuttings

## Properties of Adsorption

Correa and Ramey (1994) conducted an investigation into the theoretical aspects of adsorption in a porous medium. They discussed the conditions under which adsorption and capillary condensation occur, and developed equations to estimate the magnitude of the effects. From the point of view of geothermal reservoirs, pure adsorption is an effect that takes place at low pressure whereas capillary condensation occurs at pressures close to the saturation pressure. At intermediate pressures, the "adsorption" phenomenon is a combination of both physical adsorption and capillary condensation, and for the purposes of discussion of reservoir performance there is no real need to distinguish between the two effects. Important in the discussion of Correa and Ramey (1994) is the concept of a critical radius $r_c$, which is equivalent to the radius of space spanned by a steam molecule, $r_g$, at a given temperature and pressure. If a pore is smaller than $r_g$, then it is impossible for a vapor molecule to enter, and capillary condensation cannot take place. This places a lower limit on the occurrence of capillary condensation. The combined effects of adsorption and capillary condensation can be seen in an estimated isotherm in Fig. 5. It should be noted that the effect of the critical radius is to reverse the trend of adsorption with temperature so that the amount adsorbed increases with temperature at a given relative pressure, which is as measured in The Geysers core samples.

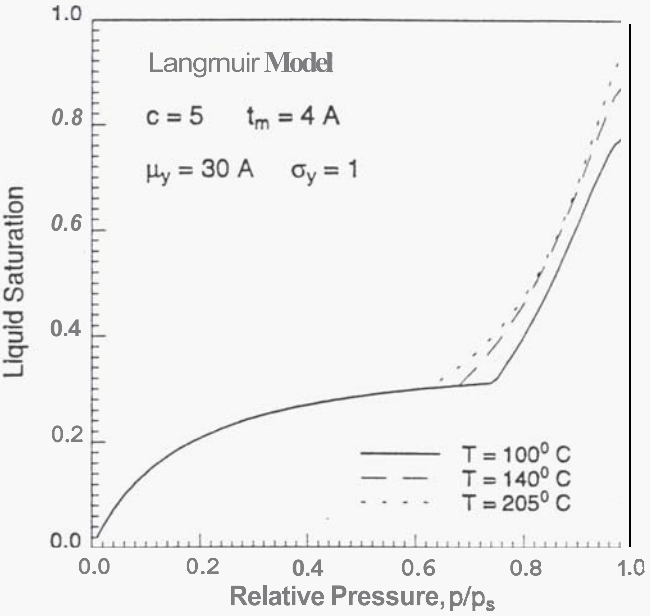
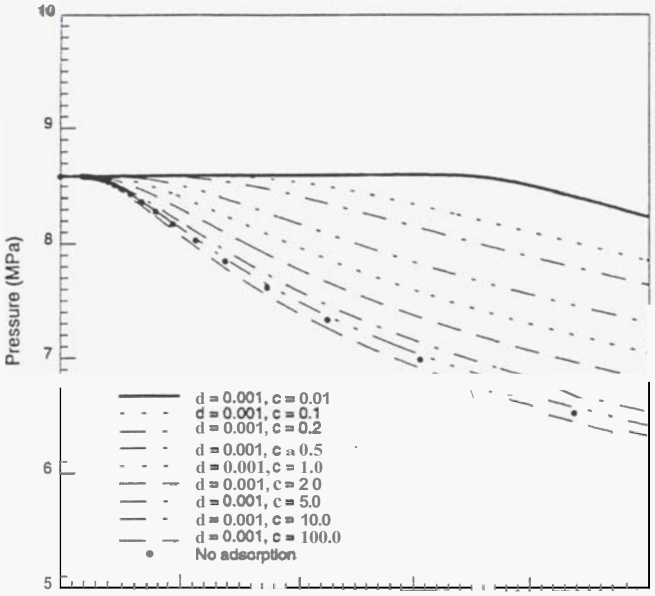


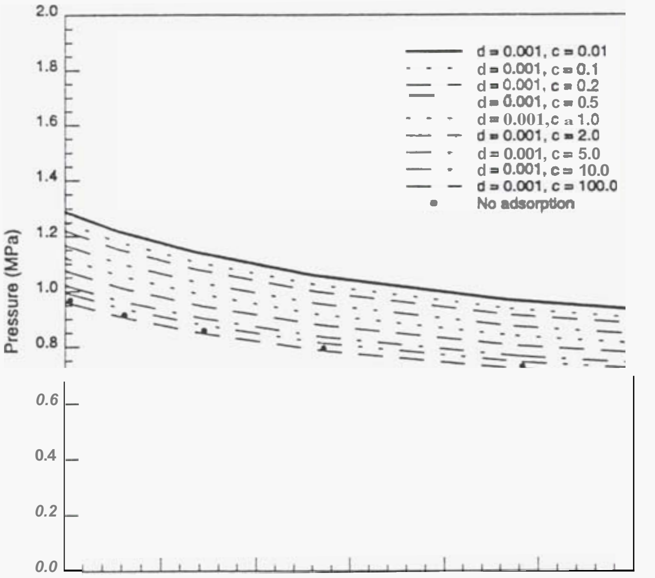
Figure 5: Theoretical Adsorption and Capillary Condensation Isotherms.

Another aspect of adsorption that required investigation was the physical properties of the adsorbed phase. Hornbrook (1994) examined density, enthalpy and heat of desorption of the adsorbed water phase. Although these properties vary somewhat from those of liquid water, Hornbrook (1994) concluded that, from the point of view of modeling geothermal reservoirs, it was acceptable to use the properties of saturated liquid water.

## Effects on Production and Injection

The effects of adsorption on geothermal reservoir performance have been discussed by Economides and Miller (1985), Ramey (1990) and Hornbrook (1994). The fundamental influence of the presence of the adsorbed phase is to support the reservoir pressure to a much larger extent than would be expected with steam alone. An example of the pressure decline in a hypothetical reservoir model with varying degrees of adsorption is shown in Figs. 6 and 7 from Hornbrook (1994).





The parameters $d$ and $c$ in Figs. 6 and 7 represent the magnitude of the adsorption and the curvature of the isotherm in a Langmuir type behavior, as described by a modified form of the Langmuir equation:

$$X = d\left[\frac{c(p/p_0)}{1+(c-1)(p/p_0)}\right] \tag{2}$$

In model calculations using measured Geysers isotherms such as the one shown earlier in Fig. 2, Hornbrook (1994) found behavior qualitatively similar to calculations using the Langmuir isotherm with $c$ values less than 1.0 (concave upward isotherms).

The effects of adsorption on geothermal reservoir production can be estimated using a simulator that accommodates the adsorption phenomenon, provided that the form of the adsorption isotherm for the reservoir formation has been measured or inferred.

The effects of adsorption on injection can be estimated using similar concepts, however it is no longer clear that adsorption is beneficial. If injection results in a local increase in pressure in the vicinity of the injection well, then the quantity of water adsorbed must increase in a manner similar to that shown in Fig. 2. This means that injected water adds to local storage of liquid in the reservoir, rather than to general production of steam. This additional stored liquid will eventually desorb as pressures decline, however this may be a long term effect that diminishes the near-term benefits of injection. For example, during the Low Pressure Area (LPA) injection test in The Geysers in 1991, Enedy, Enedy and Maney (1992) reported that $9.1\times10^8$ kg of water were injected over an area of about $3.2\times10^6$ m$^2$, resulting in a pressure increase from 1.03 MPa to 1.31 MPa. Based on Geysers adsorption measurement such as those in Fig. 2, Hornbrook (1994) estimated that about $5.2\times10^8$ kg of water were readsorbed, or about 57% of the total amount injected. Evaluation of the effectiveness of an injection scheme therefore needs to address the counteracting influences -- raising pressures will result in higher productivity in the production wells, but will cause less injected fluid to be immediately available as steam.

## Conclusions

Reservoir engineering design of production and reinjection schemes in vapor-dominated geothermal reservoirs must take proper account of the effects of adsorption. The general effect of adsorption is to support production. To estimate the extent of this support, it is necessary to make measurements of the adsorption isotherms of the particular reservoir rocks. Fortunately, it has been determined that these measurements can be made using well cuttings instead of cores. Theoretical studies indicate that adsorption should increase with temperature at a given relative pressure; this conclusion was confirmed in laboratory measurements.

Based on the measured adsorption isotherms for The Geysers geothermal field, allowing reservoir pressure to rise during reinjection may result in substantial short-term reduction in effectiveness of injection. The overall efficiency of an injection scheme needs to take this into account.

## Acknowledaments

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