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AN EXPERIMENTAL STUDY OF ADSORPTION IN VAPOR-DOMINATED GEOTHERMAL SYSTEMS

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ABSTRACT

We report results of steam adsorption experiments conducted for rock samples from vapor-dominated geothermal reservoirs. We examine the effect of the temperature on the adsorption/desorption isotherms. We find that the temperature effect is only important on the desorption such that the hysteresis becomes more pronounced as the temperature increases. The scanning behavior within the steam sorption hysteresis loop is also studied to investigate the behavior during repressurization. Collection of sets of data on the sorption behavior of The Geysers geothermal field in California is presented.

INTRODUCTION

Geothermal systems can be classified into two categories: Liquid-dominated and vapor-dominated reservoirs. Liquid- and vapor-dominated geothermal reservoirs have large and small liquid saturations, respectively. Since the resident fluid is saturated or superheated steam, the vapor-dominated geothermal systems are among the most interesting commercially. In particular, we focus on The Geysers, CA, the world's largest vapor-dominated reservoir.

In the past, there have been some attempts to explain the recharge in The Geysers geothermal field. White (1973) speculated on the two plausible mechanisms: A separate external water source and adsorption of liquid water. The first mechanism has been ruled out since further research has been unsuccessful in proving any evidence of a hidden water source, leaving adsorption phenomena as the most plausible fluid storage mechanism in The Geysers field. Therefore, to improve efficiency during injection/production projects in The Geysers, the phenomena of adsorption and its effects on the fluid flow and storage processes in such geothermal systems must be further explored. To this end, a number of studies have been initiated at Stanford to measure the amount of water adsorbed and ultimately to construct an *adsorption map* of the field. Earlier attempts were reported by Hsieh (1980) and Leutkehans (1988). A BET type sorptometer equipment was constructed and used for high temperature adsorption measurements on Berea sandstone and unconsolidated silica sands, as well as on core samples from The Geysers, CA and Larderallo, Italy. However, the accuracy of these experimental results were questioned due to the excessive leaks from the sorptometer equipment at the elevated temperatures, mainly due to the long equilibrium times required when using very tight core samples. This problem was also acknowledged by Herkelrath and O'Neal (1985) in their experimental study of water adsorption in the context of disposal of nuclear wastes. Recently, Harr (1991) and Shang et al. (1994) made an advance and conducted more accurate steam adsorption measurements on tight core samples from The Geysers, CA, by using an improved, computer-automated, high temperature sorptometer equipment.

In this paper, we report on the continuing experimental effort to examine the effects of adsorption in vapor-dominated geothermal systems, particularly The Geysers, CA. First, we describe our experimental apparatus and procedure. Next, we discuss our experimental results and illustrate sorption isotherms for various Geysers' samples at different temperatures. Finally, we shall discuss *scanning curves*, which are adsorption isotherms that span only a partial range of pressure.

EXPERIMENTAL APPARATUS

Our experimental apparatus is a computer-automated, high temperature sorptometer (built

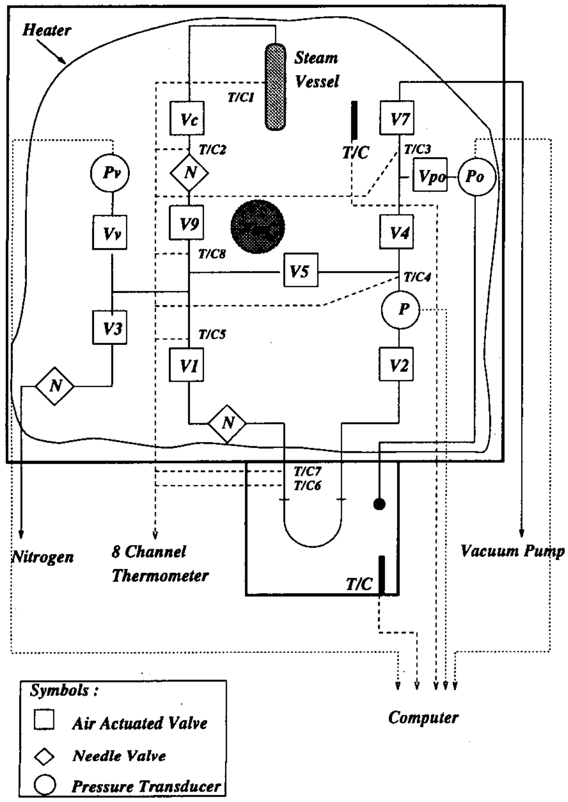

Figure 1: A schematic of the experimental apparatus.

by Porous Materials, Inc.). It consists of three isolated chambers (electronics, top and sample chambers), a computer system and a vacuum pump. All of the electronics that control the operation are located inside the electronics chamber, which is kept at room temperature. Control software loaded in the computer system is used to operate and carry out sorption experiments. A schematic of the top and the sample chambers is shown in Figure 1. As shown in the figure, the top chamber consists of a set of valves, transducers and thermocouples, a steam vessel, a heater and a fan. This chamber is kept at a temperature higher than the experiment temperature. At present, however, the temperature limitation on the equipment imposes a restriction on the maximum temperature (currently 150 °C) of this chamber. Finally, the third chamber is the sample chamber where a sample tube container is located. The sample chamber has a separate heating system such that it can be kept at the experiment temperature. Samples to be used for experiments are loaded into the sample cell (or tube). The sample cell is a stainless steel U-tube with inner diameter of 9.65 mm, restricting the size of the samples. Therefore, every core sample is crushed into smaller pieces that can fit to the sample cell. We must also note that breaking samples into smaller pieces might affect both adsorption and desorption results. However, Harr (1991) reported that the effect of crushing on the amount adsorbed is insignificant. On the other hand, considering the fact that the adsorption equilibrium time for tight core samples, such as The Geysers, with porosities of order of a few percent could be extremely long, using moderately crushed samples conveniently reduces the experiment run time and reduces the danger of leaks.

EXPERIMENTAL PROCEDURE

Since the equipment is computer-automated, the experimental procedure is simple. Normally, an operator only needs to load and start the control software. The remaining experimental procedure is carried out under computer control. Here we shall summarize the sequence. Before each experiment, a new sample is outgassed under vacuum for a sufficiently long time at an elevated temperature (normally at 180 °C). Then, the procedure followed to obtain a single point on an adsorption and a desorption isotherm is as follows: First, during adsorption, the sample cell is initially isolated from the reference volume, located inside the top chamber, by closing the valves V1 and V2 (see Figure 1). Steam is then introduced to the reference volume. Next, a pressure reading (p_i) is taken when the pressure is stabilized in the reference volume. Following this, steam in the reference cell is expanded into the sample cell by opening the valves V1 and V2 and another pressure reading (p_f) is taken when the pressure in the system is stabilized again, at which time the stage is completed by closing the valves V1 and V2. Thus, an adsorption isotherm over the entire pressure range can be obtained by repeating the above steps until the saturation pressure is reached, after which the direction of the experiment can be reversed to a desorption, if desired. During desorption, the reference and the sample cells are also initially isolated. The pressure in the reference volume is now reduced by producing a certain amount of steam. A stabilized pressure reading, again corresponding to p_i, is taken. Next is to open the valves V1 and V2 and to wait until an equilibrium pressure p_f is obtained. This gives a single point on the desorption curve. Repeating these steps until the minimum pressure value desired completes the desorption isotherm.

During an adsorption (or a desorption) stage, the amount of water adsorbed (or desorbed) is calculated from the following equation

$$X^n = X^{n-1} + (p_i^n - p_f^n)\frac{V_r}{RT_r} - (p_f^n - p_f^{n-1})\frac{V_{SC} - V_S}{RT_t}, \quad (1)$$

where $X, p_i, p_f, Vr, V_{SC}, V_S, T_r, T_t$ and R are the amount adsorbed in moles, the initial and the equilibrium pressures, the reference, the sample cell and the sample volumes, the temperatures in the top and the sample chambers, respectively. Superscripts n and $n-1$ denote the parameter values corresponding to the current and the previous stages, respectively.

DISCUSSION OF RESULTS

We carried out a series of steam sorption experiments towards the final goal of constructing an *adsorption map* of The Geysers geothermal field. We also examined the effects of temperature on steam adsorption process, and finally investigated the behavior of *scanning curves* of steam adsorption hysteresis for The Geysers' samples. Adsorption experiments were carried out for samples from five different wells located in The Geysers field. Experiments for each sample were repeated at three different temperatures (80, 100 and 120 °C). Due to the temperature restriction mentioned earlier, we have not conducted tests at temperatures higher than 120 °C. In the future, however, higher temperature experiments are planned following modifications to the equipment.

In Figures 2, 3, 4, 5 and 6, we show results obtained in steam adsorption experiments for samples from NEGU-17, Calpine Co. MLM-3, Sulphur Bank 15-D, Cold Water Creek and CCPA Prati State 12 at 80, 100 and 120 °C, respectively. The location of these wells in the field is as follows: NEGU-17 (North East Geysers Unit 17) is in the north east, MLM-3 in the south east, Prati Sate-12 and Cold Water Creek in the north west and Sulphur Bank-15D in the central west Geysers. Significant differences in the adsorption behavior of the samples studied were observed. The shape of the curves as well as the magnitude of the adsorption are quite different. For the NEGU-17 sample (Figure 2), the curve remains almost flat until a very high relative pressure value, at which point it curves upward, while a different behavior is observed for the samples from the other four locations (Figures 3-6). These other isotherms show a monotonical increase as relative pressure increases. A previous Stanford study by Shang et al. (1994) showed that adsorption behavior may

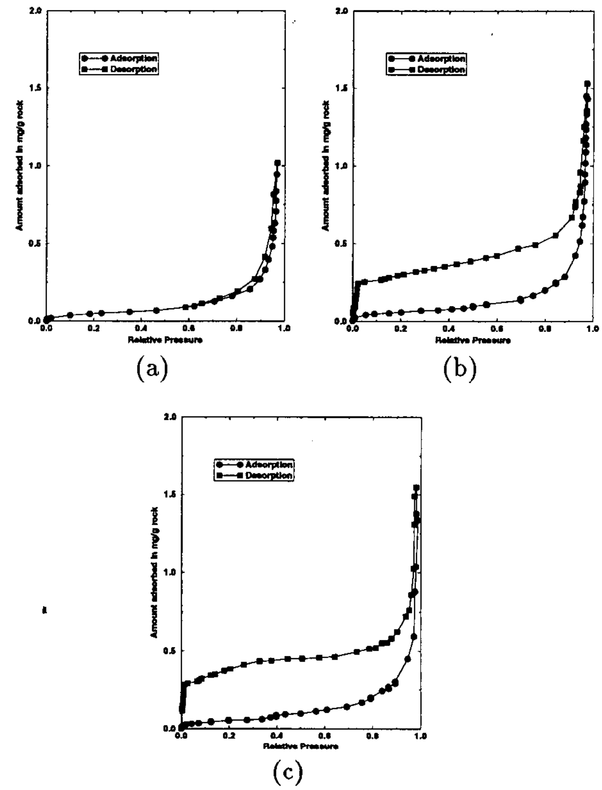

Figure 2: Results of adsorption experiments for NEGU-17 at (a) 80, (b) 100 and (c) 120 °C.

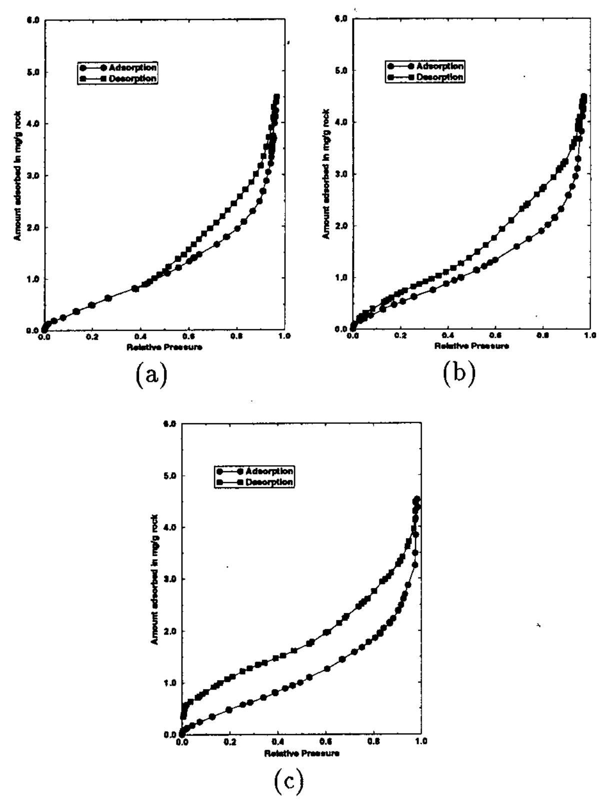

Figure 3: Results of adsorption experiments for Calpine Co. MLM-3 at (a) 80, (b) 100 and (c) 120 °C.

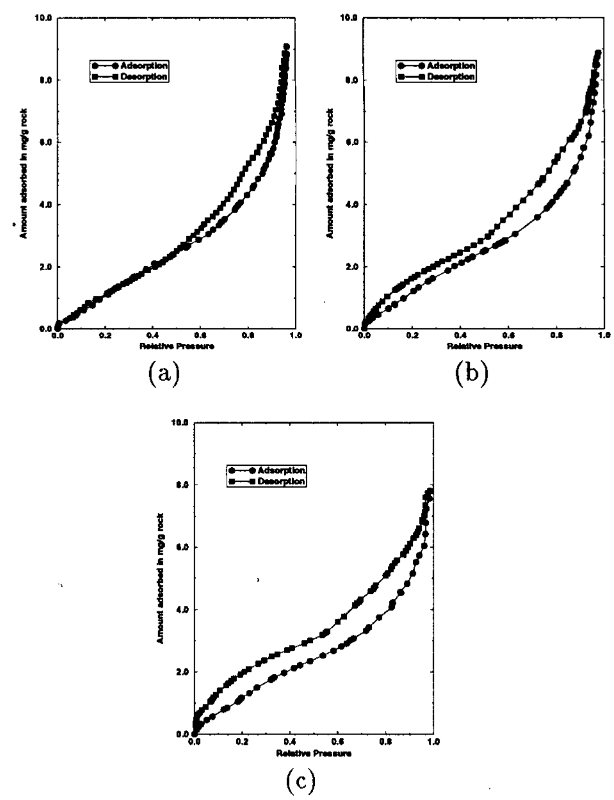

Figure 4: Results of adsorption experiments for Sulphur Bank 15-D at (a) 80, (b) 100 and (c) 120 °C.

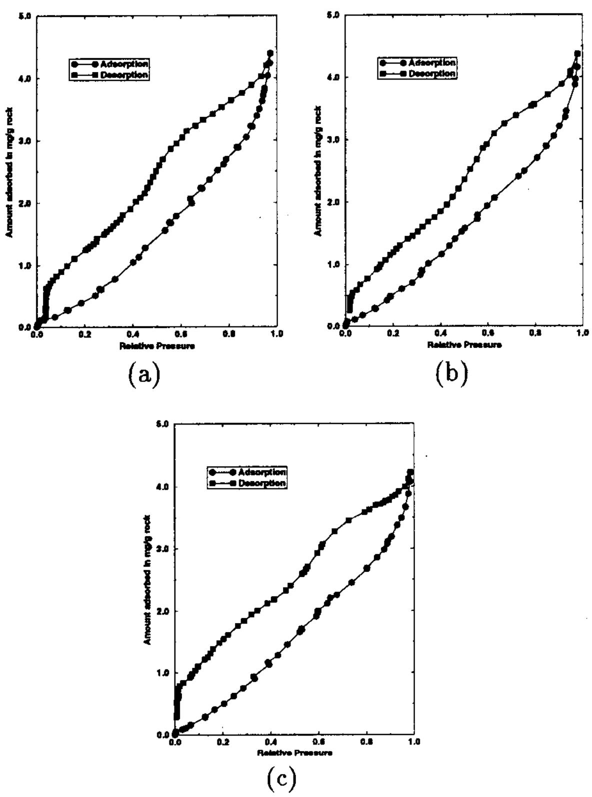

Figure 5: Results of adsorption experiments for Cold Water Creek at (a) 80, (b) 100 and (c) 120 °C.

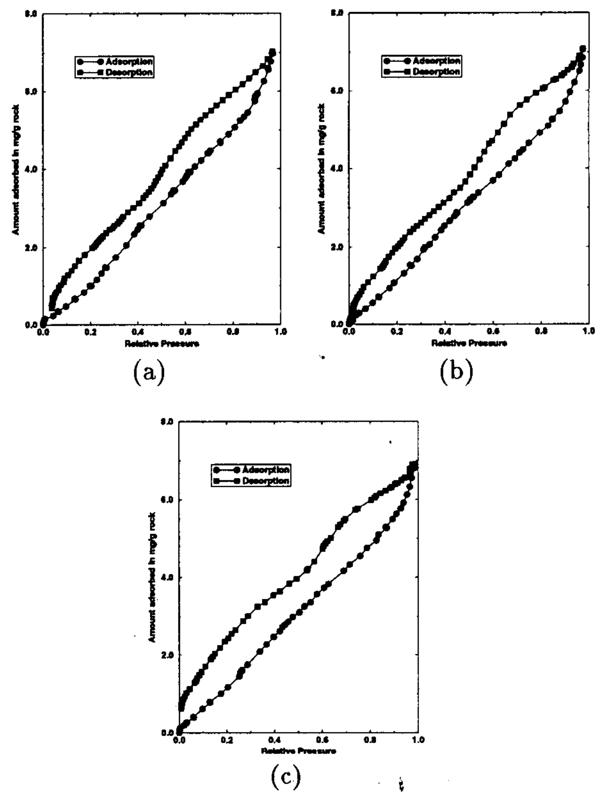

Figure 6: Results of adsorption experiments for CCPA Prati State 12 at (a) 80, (b) 100 and (c) 120 °C.

differ even for samples obtained at different elevations in the same well. At this point, our preliminary results are not conclusive since the experimental data do not cover the whole field. However, they indicate a need for further research in this area. Therefore, in order to have a better understanding of the adsorption behavior in The Geysers geothermal field, more adsorption experiments are required from additional locations.

An interesting and rather unusual feature observed in the results shown in Figures 2-6 is the temperature effect. The figures indicate that the temperature has a very important effect on the desorption curve while it has only a slight effect on the adsorption. The temperature effect on the desorption curve is such that the hysteresis loop becomes more pronounced (Figures 2-4) as temperature increases. Moreover, the shape of the adsorption-desorption loop is very different than that previously reported for other sorption experiments in other porous solids. The difference is that the hysteresis here persists until a very small pressure value (of order of 0.001 *psia*) leaving a residual amount adsorbed, whereas it is normal for hysteresis to cease at a moderate pressure value. Furthermore, experimental results for samples from Cold Water Creek (Figure 5) and Prati State 12 (Figure 6) show a different temperature effect, limited only to small pressure values. This effect is of importance because it controls the hysteresis loop. From our results, we conjecture that the temperature effect on the hysteresis will be even more pronounced at higher temperatures than those we studied. Recently, Satik and Yortsos (1995) have made an attempt to explain this effect by modelling the process with the use of a pore network model and combining it with the improved adsorption theory of Evans et al. (1986) for narrow pores and also with a model proposed by Parlar and Yortsos (1988). Satik and Yortsos (1995) compared their numerical simulation results with our experimental findings and found a good agreement. To explain the temperature effect observed in our experiments, their results suggested that, for adsorption in microporous solids, liquid occupying narrow pores (of order of 1 *nm*) can behave in a supercritical state as the temperature exceeds a critical value. Such fluids, depending on the topology of the porous medium, can actually prevent the liquid occupying larger pores from evaporating due to the lack of their accessibility to vapor, delaying evaporation (desorption) until very small presure values.

Finally, in Figure 7, we show *scanning curves* obtained for a sample from NEGU-17 at 120 °C. *Scanning curves* are obtained by changing the direction of the experiment from an adsorption to a desorption at an earlier pressure for each loop. As seen from the figure, the starting pressure value for each loop is the same, at a complete vacuum. Figure 7 also shows that hysteresis diminishes as the final pressure value for a loop decreases. A complement to this type of *scanning curve* is to start the adsorption part at larger pressure value for each loop and to finish it always at the saturation pressure. However, the second type of curve requires changing the direction of the experiment from a desorption to an adsorption at a larger pressure value for each loop. At present, only the first type of the curves can be obtained because our sorptometer equipment can not handle the sequence of steps required for the second type. With a further modification to the control software, we also expect to obtain the second type of curves in the near future. The two types of *scanning curves*, when combined together, should reveal information important to the optimization of injection-production strategies in The Geysers geothermal field.

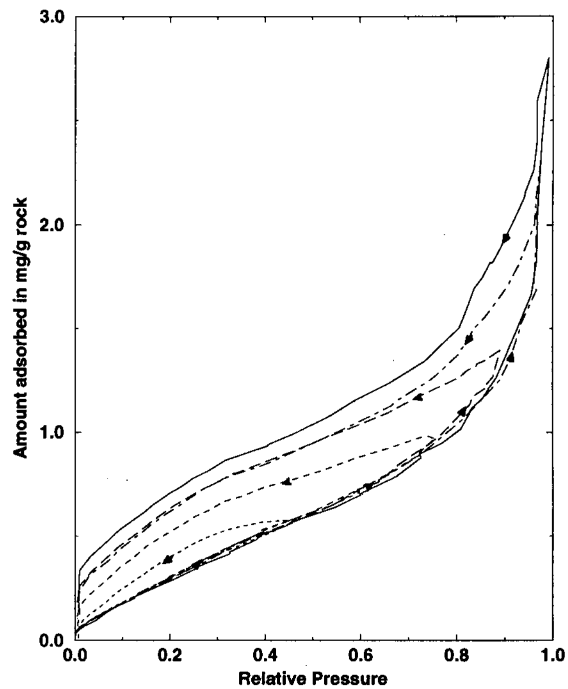

Figure 7: Scanning curves obtained for a sample from NEGU-17 at 120 °C.

CONCLUSIONS

In this paper, we have reported our results of sorption experiments conducted for samples from The Geysers geothermal reservoir, CA. We have studied the effect of the temperature on the adsorption/desorption cycle. Our results have shown that the effect of temperature is insignificant on the adsorption whereas it is very important on the desorption, therefore, a more pronounced hysteresis behavior is observed as the temperature inceases. We also conjectured that this effect can even be more pronounced at larger temperature values than we examined. To have a better understanding of the phenomena, however, more experiments at elevated temperatures are required. Finally, we studied the behavior of *scanning curves* and presented a family of *scanning curves* of the hyteresis for a sample from The Geysers field.

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