

EXPERIMENTAL STUDY OF WATER ADSORPTION ON GEYSERS RESERVOIR ROCKS

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ABSTRACT

Experimental isotherms of water vapor adsorption/desorption on three geothermal reservoir rock samples have been measured at temperatures of 80, 100, 120 and 140°C. Initial surface status of the sample was found to influence the amount of water adsorbed. At low relative pressures, adsorption is the dominant process of water retention onto the rock samples. Adsorption/desorption hysteresis was observed to exist over the whole pressure range at all temperatures. Similar observations were made for all three samples. The results of this study suggest that adsorption is important in storing water in geothermal reservoir rocks not only in itself, but also in inducing capillary condensation.

INTRODUCTION

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 reasonable. As pointed out by Ramey (1990) that if the only mechanism for liquid storage is adsorbed water, then the desorption curve provides important information for performance matching and production forecasting. It is therefore obvious that measurement of adsorption/desorption 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.

Water vapor desorption was regarded as a simple and reliable technique in core analysis by Melrose (1988). In a comprehensive study to determine capillary pressure in the low-saturation region, Melrose (1991) compared results obtained using different techniques, and concluded that water vapor desorption method gave capillary pressure in good agreement with those obtained using the centrifuge and the porous plate methods. However, it should be pointed out that water vapor desorption in this case referred to the part of the desorption curve at relative pressures greater than 0.9,

and the corresponding saturations are higher than 3.3% for the Berea sandstones studied by Melrose (1988). At high relative pressures, adsorption is accompanied and complicated by capillary condensation, and it is likely that water held by capillary force constitutes a large part of the desorbed water.

Literature on water adsorption has been largely concerned with pure adsorbents, with carbon and silica being the most popular (Dubinin, 1980, Stoeckli, et al., 1983). The majority of the water adsorption studies are associated with the characterization of porous material. Willems et al. (1988) reported studies of water adsorption on hardened cement pastes and observed large adsorption/desorption hysteresis at 25°C. Carrott et al. (1991) studied water adsorption on synthetic zeolites in order to elucidate the relative influence of surface chemistry, pore size and pore shape upon the form of the water adsorption isotherm. A common feature of these studies is that the adsorption tests were all made at low temperature (between 0 to 25°C) and some special behaviors of water (Gregg and Sing, 1982) were observed.

Reservoir related water adsorption investigation is limited, particularly at high temperatures. Hsieh (1981) constructed a BET type of apparatus for high temperature water adsorption measurements. He conducted a number of adsorption measurements on Berea sandstone and unconsolidated silica sand. Conclusions reached in his study were that adsorbed water is an important source of steam in vapor dominated geothermal systems and that water vapor pressure lowering in a rock is dominated by micropore adsorption (Hsieh and Ramey, 1983). Luetkehans (1988) continued Hsieh's research by improving the apparatus. Measurements of N₂ adsorption were made for Berea sandstone, cores from the Geysers, California, and Larderello, Italy. Water adsorption/desorption tests were also conducted. However, the true magnitude of the amount adsorbed was suggested to be 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 the experimental error. Laboratory studies of water adsorption on porous media were also conducted by Herkelrath *et al.* 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 II, 1985). They reported similar findings to those by Hsieh and Ramey (1983). Linear adsorption isotherms were claimed to fit data on Topopah Spring welded tuff up to a relative vapor pressure of 0.9. The problem of leakage in long equilibrium time was also identified in their work.

Clearly, there was a need to improve the apparatus in order to obtain reliable data of water adsorption at high temperatures. Harr (1991) performed preliminary investigation on the use of an automated sorptometer from Porous Material Inc. (PMI) for high temperature water adsorption measurements. To our knowledge, this is the first commercial sorptometer built for high temperature adsorption tests. Considerable time was spent to investigate various problems associated with the sorptometer both by Harr and in the present study.

APPARATUS AND PROCEDURES

The sorptometer consists of basically three parts. (1) a set of valves and pressure transducers kept in a high temperature chamber, (2) a sample chamber for loading and unloading samples, and (3) the electronic part for automatic control. During normal operation, the operator only needs to load the sample and the rest of the procedures are accomplished via a computer keyboard.

The principle of the adsorption/desorption measurement is the same as a BET type of experiment. The quantity one measures is the pressure of water vapor in the system before and after adsorption/desorption. System volumes are predetermined by expanding N_2 and measuring the corresponding pressures. The amount adsorbed/desorbed can then be calculated from mass balance. Knowing the weight of the rock sample, we can obtain the amount of water adsorbed per unit weight at a given pressure.

Due to the limitation of the size of the sample holder, rock samples had to be broken into granulars with equivalent diameters of approximately 8mm. New samples were all heated at 180°C under vacuum overnight to get rid of any surface residuals before running the adsorption test. Upon adsorption, water vapor is added incrementally to the system from a steam reservoir, which is kept at a temperature higher than the test temperature, and time was allowed for the system to reach equilibrium. Desorption commences at the end of adsorption test. In this case, water vapor is gradually pumped away until the adsorbed water is completely desorbed. The sample is reweighed at the end of the tests.

RESULTS AND DISCUSSION

The experimental studies reported here are the results of water adsorption/desorption tests performed on Geysers shallow reservoir core, Monteverdi well #2 rock and Berea sandstone using the PMI sorptometer. As

mentioned previously, the size of the rock samples used for an adsorption test is limited by the geometry of the sample holder. 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. Knowing the complexity of the adsorption process, it is important to ensure that the rock surface has the same condition prior to each adsorption/desorption isotherm test. This was achieved by heating the sample at 180°C under vacuum for 3 to 4 hours. Reproducible isotherms were obtained after this pretreatment.

Figures 1 to 3 show the adsorption/desorption isotherms obtained at 120°C for Geysers shallow reservoir core, Berea sandstone and Monteverdi #2 sample, respectively. As shown in the figures, the amount of water adsorbed at a relative pressure of 0.7 is 1.3mg/g for Geysers shallow reservoir core, 1.0mg/g for Berea sandstone and 0.5mg/g for Monteverdi #2 samples. These quantities agree reasonably well with data

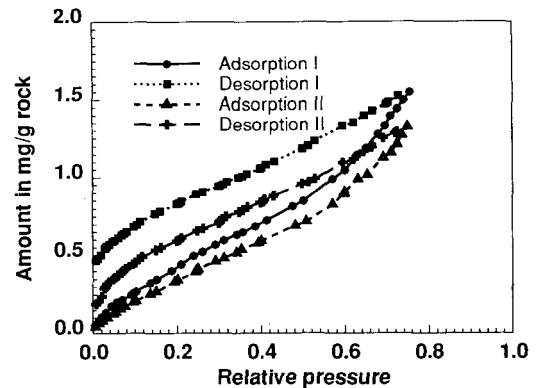


Figure 1 Isotherms on Geysers Shallow Reservoir Core

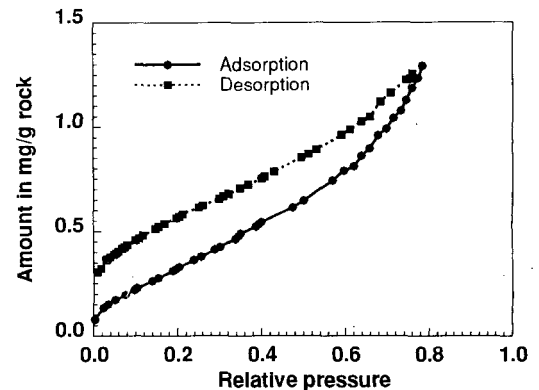


Figure 2 Isotherms on Berea Sandstone

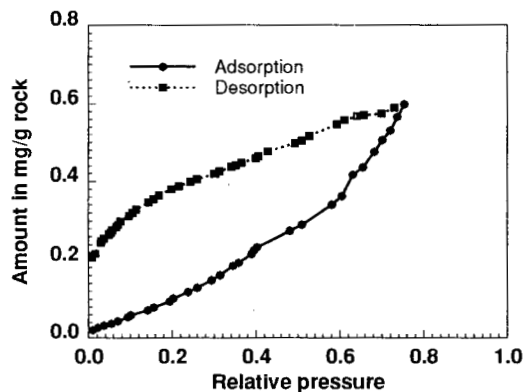


Figure 3 Isotherms on Monteverdi #2 Core

obtained by Hsieh (1980) and Luetkehans (1988). There is an obvious adsorption/desorption hysteresis in each case, and it exists at near zero pressure. In Figure 1 are two sets of adsorption/desorption isotherms from two tests. The difference between these tests are that test II was performed without pretreating the sample, i.e. starting the second adsorption test at the end of the first desorption cycle. Comparison of the two sets of isotherms indicates the presence of irreversible adsorption.

Adsorption/desorption hysteresis

It is clear that significant hysteresis exists for steam adsorption/desorption on all samples tested. As shown by scanning electron micrographs (SEM), all the rock samples have complicated physical structures. This physical heterogeneity of the rock must be responsible for the presence of the adsorption/desorption hysteresis. Capillary condensation provides a basic explanation of the phenomena at high relative pressures (Adamson, 1990), and it can be quantitatively described using network models while applying the Kelvin equation to both adsorption and desorption isotherms (Mason, 1982, 1988)

However, hysteresis exists at very low relative pressures in the samples tested in this work. A plausible explanation for this behavior is that irreversible changes may occur in the pore structure on adsorption so that the desorption situation is different from the adsorption one (Bailey et al., 1971). For the adsorption of water at high temperatures, it is likely that the interaction of polar water molecules with rock surface causes irreversible adsorption at low relative pressures, i.e. there is some weak chemisorption for the first monolayer. Weak chemisorption of water onto cement pastes was reported by Willems *et al.* (1988) at room temperature. The observed low pressure hysteresis in this work is at least partly caused by weak chemisorption. The repeated tests without pretreatment in between provide some support for this assumption. Evacuation at test temperature mainly removes physically adsorbed water. So for the

subsequent test, the surface of the sample was partly, if not completely, covered by chemisorbed water molecules. Thus, the amount of water adsorbed in the subsequent tests is smaller than that for the first one, and the amount of water retained at the end of desorption isotherms was also reduced.

Due to the presence of adsorption/desorption hysteresis, the measured desorption isotherms can be very different from the adsorption one. Understanding of the hysteresis phenomena bears significance to the reinjection process since the desorption isotherm is directly related to steam production in geothermal reservoirs.

Adsorption and capillary condensation

Adsorption is a surface phenomena and is affected not only by the surface area of the material but also by its chemical composition. Capillary condensation is related to the geometry of the porous media and for a given adsorbate it only depends on the geometric structure of the porous material. These processes are similar in nature, i.e. they both cause vapor to condense onto the solid. They are related in such a way that adsorption provides a precursor for capillary condensation. One can divide the physical processes of adsorption in porous materials 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 (pore diameters not exceeding 20 Å), the pore space will be filled up (commonly termed as volume filling) before multilayer adsorption is developed. What happens physically is that as multilayer adsorption develops, the micropores become filled by a meeting of the adsorbed molecules from opposing walls. In large pores, multilayers of adsorbed water form as pressure increases. In reservoir rocks, there exist pores of different shapes and sizes. Due to the variation in pore size, capillary condensation occurs at different relative pressures. Since it is difficult to obtain the actual pore size distribution, it is hard to tell at what pressure capillary condensation will take place. Volume filling exists to a small extent in the rock samples studied in this work, and this suggests the presence of micropores in the rocks. However, the percentage of the micropores must be small judging from the shape of the adsorption isotherms. Thus, volume filling is not considered in the present discussion.

Figure 4 shows adsorption isotherms on the three rock samples obtained at 80°C. At relative pressure below 0.6, the amount of water adsorbed can be approximated by a linear function of relative pressure in all three 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 adsorption

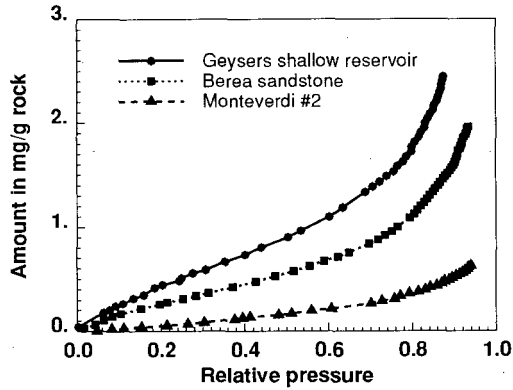


Figure 4 Comparison of Adsorption Isotherms at 80°C

isotherm is an indication that capillary condensation takes place and its contribution to total water retention onto the reservoir rock becomes more significant as pressure is further increased.

Due to equipment problems, we have not yet been able to obtain reliable data at relative pressures greater than 0.9 for higher temperatures. Based on the above discussion and the experimental data at 80°C, we expect similar adsorption/condensation phenomena for higher temperatures. The magnitude of water retention is yet to be measured.

Effect of temperature on water adsorption

Figures 5 to 7 show comparison of adsorption isotherms at different temperatures obtained on Geysers shallow reservoir core, Berea sandstone and Monteverdi #2, respectively. The effect of temperature on the amount of water adsorbed varies from sample to sample. For Geysers shallow reservoir core and Berea sandstone, as shown in Figures 5 and 6, appreciable changes in the amount of water adsorption did not occur until the relative pressure reached 0.65. However, for the Monteverdi #2 sample, considerable difference appears at very low relative pressures, and this difference increases as the relative pressure increases, as shown in Figure 7. The reason for the different temperature dependence is not clear.

Salt in solution has long been considered to cause the low vapor pressure of water in vapor dominated geothermal systems (Ramey, 1990). So far in our discussion, we have ignored the possible effect of salt on water retention and vapor pressure lowering. We believe that if there are minerals present in the rock sample, they will dissolve in the adsorbed water film and influence the adsorption/condensation process.

CONCLUSIONS

Adsorption is important in geothermal reservoirs, not only in itself but also in inducing condensation to take

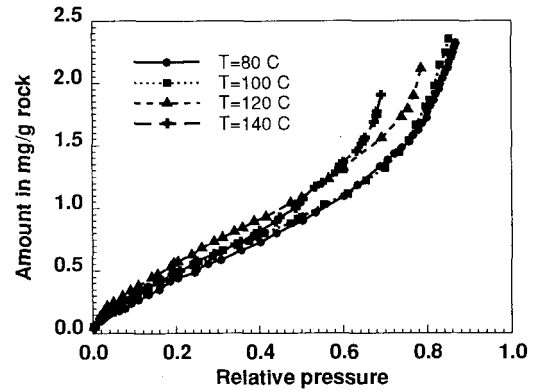


Figure 5 Comparison of Isotherms on Geysers Shallow Reservoir Core

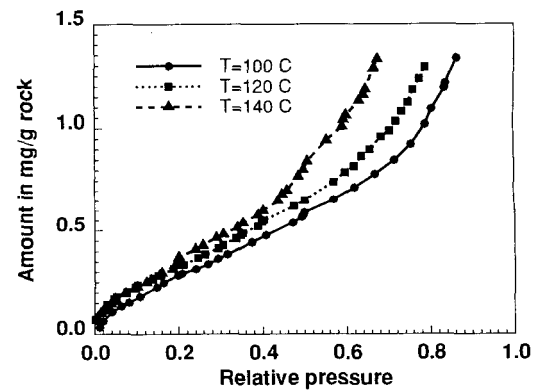


Figure 6 Comparison of Isotherms on Berea Sandstone

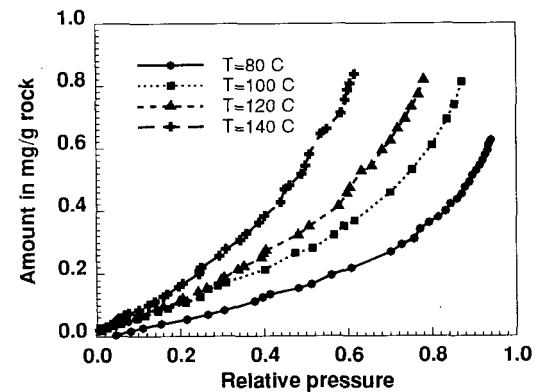


Figure 7 Comparison of Isotherms on Monteverdi #2 Core

place easier than in the absence of adsorption. It is logical to suggest that the system is adsorption dominated at lower relative pressures, and changes to capillary condensation dominates as pressure increases. Both adsorption and capillarity cause vapor pressure lowering.

However, it is hard to determine the cause of this vapor pressure lowering since the status of the rock surface is largely unknown.

Significant hysteresis exists for water adsorption/desorption on the rocks tested and it is shown to be caused, at least partly, by weak chemical interaction. The amount of water adsorption is affected by temperature and its effect is found to be sample dependent.

Much work needs to be done to measure the amount of water adsorbed/condensed at higher relative pressure. Additional work will be undertaken to investigate the possibility of running adsorption test at temperatures higher than 140°C so that we can simulate geothermal field conditions as closely as possible.

There is an obvious need to develop a model to describe the adsorption-capillary condensation process. The combination of Frenkel-Halsey-Hill (Halsey, 1952, Adamson, 1990), used for adsorption, and the Kelvin equation, used for capillary condensation, provides a good basis for such a model. Current work on this subject is in progress.

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