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HIGH TEMPERATURE WATER ADSORPTION ON THE GEYSERS ROCKS

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ABSTRACT

In order to measure water retention by geothermal reservoir rocks at the actual reservoir temperature, the ORNL high temperature isopiestic apparatus was adapted for adsorption measurements. The quantity of water retained by rock samples taken from three different wells of The Geysers geothermal reservoir was measured at 150 °C, 200 °C, and 250 °C as a function of pressure in the range $0.00 \le p/p_0 \le 0.98$, where p_0 is the saturated water vapor pressure. Both adsorption (increasing pressure) and desorption (decreasing pressure) runs were made in order to investigate the nature and the extent of the hysteresis.

Additionally, low temperature gas adsorption analyses were performed on the same rock samples. Nitrogen or krypton adsorption and desorption isotherms at 77 K were used to obtain BET specific surface areas, pore volumes and their distributions with respect to pore sizes. Mercury intrusion porosimetry was also used to obtain similar information extending to very large pores (macropores). A correlation is sought between water adsorption, the surface properties, and the mineralogical and petrological characteristics of the solids.

INTRODUCTION

This project has been undertaken in order to expand our understanding of the adsorption/desorption processes occurring in rocks found in geothermal reservoirs, with the intention of using such information in improving the efficiency of the recovery of geothermal energy. The results of the water retention measurements can be used as one of the inputs to geothermal reservoir models. The main goals were:

- to measure water retention by the reservoir rocks at temperatures approaching the actual reservoir conditions and to explore the temperature dependence of adsorption;
- to investigate the hysteresis behavior;
- to characterize the rocks included in the study with respect to water adsorption capacity;
- to research the possibility of estimating this capacity using available properties of the rocks.

Such properties as porosity, BET specific surface area, total pore volume and pore volume and area distributions with respect to pore size can be obtained by methods that are standardized and relatively inexpensive in contrast to high temperature water adsorption measurements.

Since the vapor pressure in vapor-dominated geothermal reservoirs in their undisturbed state is equal to the saturation pressure of liquid water at the measured reservoir temperature, the reservoir must contain some amount of free water present in wide pores and fractures (Pruess and O'Sullivan, 1992). The steam drawn from such a reservoir initially comes from the evaporation of this water. After the reserve of this free water is exhausted, the water retained in smaller pores and adsorbed on the surfaces will start to evaporate, and the pressure will decline. The process of depletion of a steam-dominated reservoir assuming thermodynamic equilibrium in all its volume (no flow restrictions) is shown schematically in Figure 1. The flat (nearly horizontal) part of the solid curve in Figure 1 illustrates that it is impossible to estimate the amount of water initially present in the reservoir by measuring the reservoir pressure, since the withdrawal of large amounts of water at this stage will be associated with a very small decline

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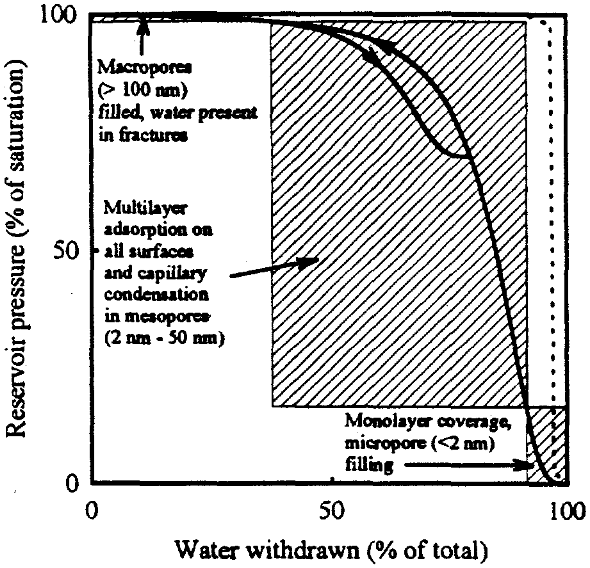

Figure 1. Pressure decline during depletion of a vapor-dominated geothermal reservoir.

in pressure. In the later stages of the reservoir operation the amount of water left in the reservoir can be determined, if water retention capacity as a function of pressure is known for the rocks found in the reservoir.

As seen in Figure 1, the reservoir pressure observed with adsorption present (solid curve) will be lower than the pressure without adsorption (dotted curve) in the later stages of the reservoir operation. With any mechanism of lowering water activity (either interactions with solid surfaces or with dissolved substances present) a gradual decline in pressure will be observed instead of an abrupt fall to zero when all the water is withdrawn. Since the decline in pressure tends to slow down a further depletion, water pressure lowering acts as a mechanism stabilizing geothermal reservoirs, by delaying a complete dry-out. This aspect can be depicted as the presence of a 'capillary suction' which keeps the moisture inside the rocks at the conditions where liquid water would quickly evaporate. The increased interest in adsorption properties of the geothermal reservoir rocks is then parallel to the increased interest in the behavior of vapor-dominated geothermal reservoirs in the later stages of their exploitation, when the pressure is substantially lower than the saturation pressure at the nominal reservoir temperature.

It should be emphasized that the transition between bulk water and the water that is held by interactions with the solid surface is gradual. The division of the relative pressure range into the subranges (Figure 1) corresponding to the formation of a multilayer, micropore filling, multilayer adsorption, and capillary condensation is not rigorous, since in some pressure ranges these mechanisms of water retention are present simultaneously, and they smoothly transform into each other. Since the fluid-solid interactions are not fully understood at the molecular level, different models are used for description of different regimes of liquid retention on solid surfaces. In all cases, the macroscopic result of the liquid-solid interaction is the change in the retained liquid's activity as compared to pure bulk liquid.

EXPERIMENTAL

Apparatus

The ORNL high-temperature isopiestic facility is a unique apparatus capable of accurate measurements (typically ± 1mg) of the change in mass of twenty 2-18 g samples simultaneously under high temperature and high pressure conditions (Holmes *et al.*, 1978). This ability makes it possible to measure water retention by materials characterized by relatively small surface areas like The Geysers rocks. The samples are placed inside a high-pressure, high-temperature autoclave in pans fitting in holes in a steel disk which can be rotated by the operator. The pans are placed in turn on the torsion suspension electromagnetic balance and weighed *in situ* by adjusting the electric current through the balance coil. The null point is detected by an optoelectronic system using a collimated light source, a dual photoresistor and a servoamplifier. The current through the coil that is required to bring the balance beam back to the null point is recorded. Figure 2 shows a schematic diagram of the experimental setup.

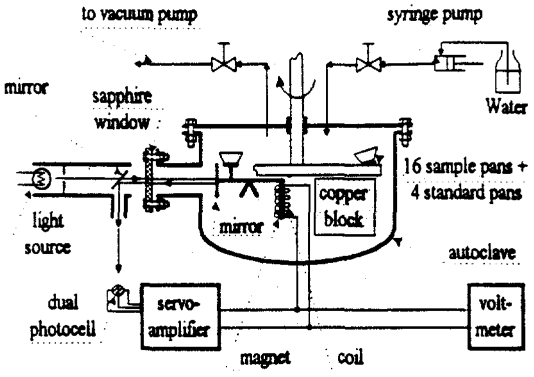

Figure 2. Schematic of the isopiestic apparatus with torsion suspension balance and optoelectronic null detector for in situ weighing.

In contrast to the most commonly used sorptometers, the quantity measured using this apparatus is the change in the mass of the solid instead of the change in the vapor pressure caused by adsorption or desorption The mass is measured by comparison with a set of standard weights placed inside the pressure vessel together with the samples. This method makes the results particularly reliable and free of large systematic errors. The densities of the samples, which have to be known in order to correct for the effect of buoyancy, can be measured inside the autoclave by weighing the samples in vacuum and then in the atmosphere of a compressed gas of known density (e.g. Ar). The samples may be left under the same vapor pressure for many days and the change of mass with time can be continuously monitored. The experimental details and procedures were described previously (Gruszkiewicz *et al.*, 1996).

Samples

The measurements were performed on core samples taken from the producing steam reservoir. Well numbers and approximate footages were as follows:

- NEGU-17, 8530-8530.5 ft (rubble)
- Prati State 12, 6261.7-6261.8 ft
- MLM-3, 4336-4336.3 ft.

The rocks were crushed and sieved. Three fractions were prepared of each sample with the following grain sizes: 2.00 - 4.25 mm ('coarse'), 0.355 - 2.00 mm ('medium'), and 0 - 0.355 mm ('fine').

The densities of the rock samples were close to each other and equal on average to 2.775 ± 0.03 g/cm^3. Both density determinations by measuring the effect of buoyancy in argon and by mercury porosimetry indicated that the density of the NEGU-17 well samples might be higher than that of the other two wells by up to 0.03 g/cm^3. This difference is smaller than could be expected if the significant differences in mineralogy and in specific surface areas of the three metagraywackes, as discussed below, are taken into account.

RESULTS

Temperature dependence and hysteresis

Figures 3 and 4 show the experimental results for water retention on the medium fractions of NEGU-17 and MLM-3 rocks, respectively, at 150, 200 and 250 °C. The physical adsorption on these rocks shows the following features:

- there is essentially no temperature dependence of the adsorption branches,
- as the temperature increases the hysteresis loop narrows in both the amount of the adsorbate and the pressure range,
- water retention is reversible,
- the hysteresis loops persist to very low pressures in the case of MLM-3, but distinct closure points are present in NEGU-17.

While on the adsorption branch the water is present both as multilayer adsorbate and as capillary condensate, in principle all of the excess retention on the desorption branch is due to capillary condensation. This explains why water retention on the desorption branch decreases with increasing temperature, while the adsorption branch is nearly temperature independent. Both the pressure range of the hysteresis loop and the excess water retention should decrease with increasing temperature, since capillary

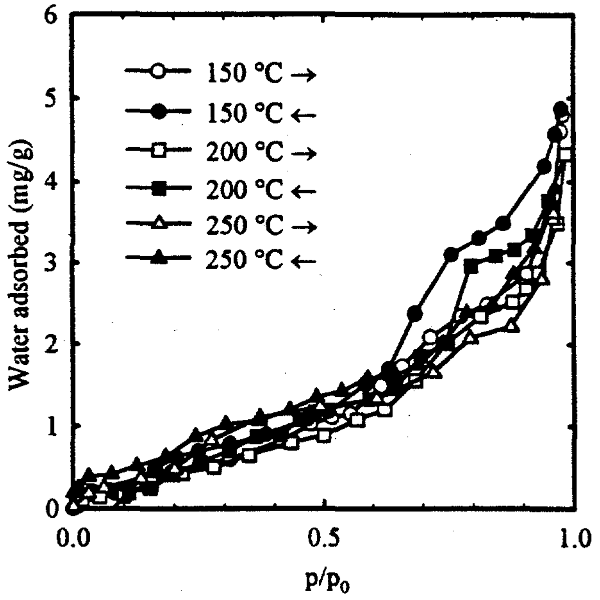

Figure 3. Adsorption/desorption isotherms of water on the medium fractions of the NEGU-17 medium grain size sample.

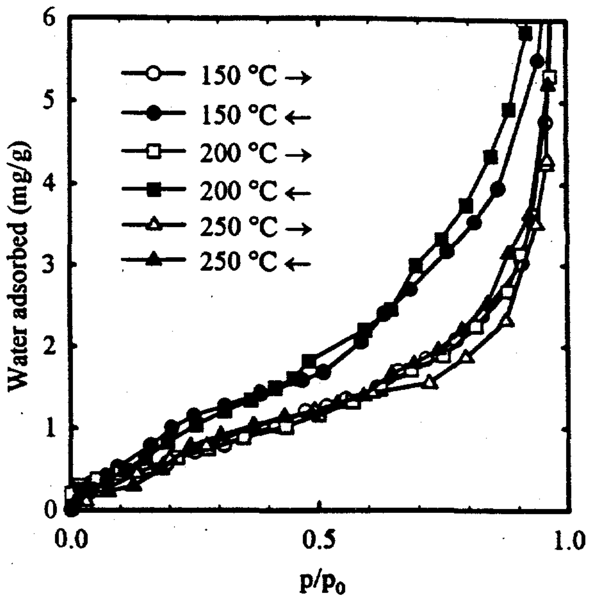

Figure 4. Adsorption/desorption isotherms of water on the medium fractions of the MLM-3 medium grain size sample.

condensation depends strongly on temperature. An analysis of the Kelvin equation,

$$\frac{p}{p_0} = e^{-\frac{4K(T)}{d}}, \qquad K(T) = \frac{\gamma(T)\, V_m(T)}{RT}, \quad (1)$$

indicates that for a constant pore diameter d, the changes in the surface tension γ, and the molar volume of the liquid V_m accompanying the increase of the temperature T would cause an approximately linear increase of the corresponding relative pressure p/p_0. According to equation 1 applied to water, the capillaries smaller than d = 20 Å (2 nm) should be filled with water at relative pressures equal to at least

$$\left(\frac{p}{p_0}\right)_{2\,\mathrm{nm}} = 0.297 + 0.00187\,t \qquad (2)$$

where t is the temperature in °C. The relative pressures calculated from equation 2 agree well with the experimentally observed inception points for the hysteresis loop at 150 °C and 200 °C. At 250 °C the hysteresis loops are very narrow, and the inception points are not well defined (Figures 3 and 4).

Since the mechanism of water retention on the adsorption branch is mainly multilayer adsorption, with a heat effect similar to that of condensation into bulk water, there is little or no change of the amount of water adsorbed this way with temperature. Since the activity of the adsorbate changes with temperature in the same way as the activity of free water, p/p_0 remains constant. It should be noted that the shapes of adsorption isotherms obtained from the Kelvin equation for capillary condensation and from the BET equation for multilayer adsorption can be very similar, so that it is not possible to distinguish between the two regimes on the basis of the isotherm shapes at one temperature.

The causes for the low-pressure hysteresis on very heterogeneous rock samples are hard to identify definitively. Certainly some of the components found in the altered graywacke show this behavior, which was previously found (Gregg and Sing, 1982) to be due in some cases to the solid structure changes(swelling) caused by the adsorbate or to reversible hydroxylation-dehydroxylation. Low-pressure hysteresis of water on calcite was observed (Gregg and Gammage, 1972) and attributed to the penetration of water into the lamellar solid, with some dissolution. The presence of solutes in the adsorbate water could additionally shift the isotherm to lower pressures.

Irreversible water retention

Apart from the reversible adsorption, illustrated in Figures 3 and 4, and found mainly in the coarse and medium fraction samples, extensive irreversible water retention was observed in the small grain size samples. Figure 5 shows that the amount of water irreversibly bound by solid minerals can be very large compared to the capacity of the porous rock structure for physical and reversible chemical adsorption. It is interesting that at least part of the irreversible water retention, whether it is referred to as chemical adsorption or mineral alteration, occurs only on fresh surfaces formed by milling, since it was not observed on coarse and medium size samples. It is also possible that the mineral with the most capacity for bonding water is occluded as small grains in other materials, so that before milling it is not accessible to vapor. The milling process can also produce fine cracks in the crystals, where water is trapped very firmly (Gammage and Gregg, 1972).

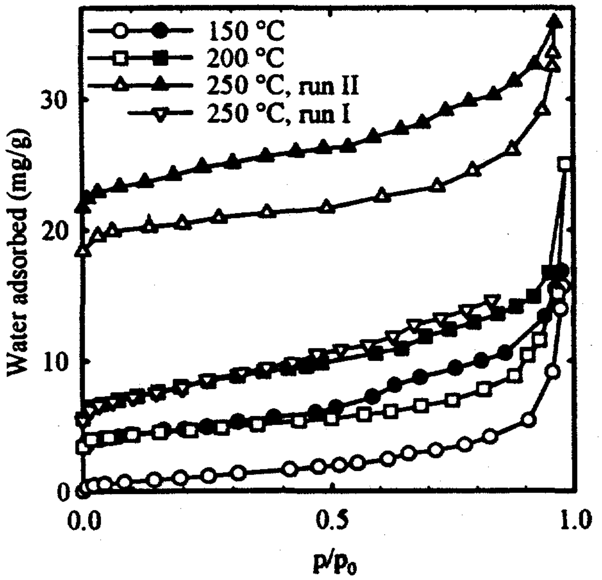

Figure 5. Adsorption/desorption isotherms of water on the small grain size fraction of the MLM-3 metagraywacke.

SEM photomicrographs of the surface of the rock samples have shown the presence of large clusters of long crystals (needles) of an alteration mineral identified by X-ray diffraction as prehnite, $Ca_2Al_2Si_3O_{10}(OH)_2$. The occurrence of these clusters is rather sporadic, but is much more abundant in the samples examined after the high temperature adsorption experiments. Similar fibrous material found in samples of cores from the same The Geysers wells as in this study was previously identified as actinolite. (Hulen *et al.* 1991)

Nitrogen and water adsorption, mercury intrusion, and rock compositions

Water differs from neutral adsorbates, such as nitrogen, in polarity, the presence of hydrogen-bond bridges, and the ability to form chemical bonds with the mineral surfaces, or even react with the bulk of the minerals, so that crystal structures are altered. These differences will certainly have an impact on the measured adsorption isotherms and specific surface areas determined from nitrogen and water adsorption. It is known that the porous material's capacity for water adsorption can be either larger or smaller than its capacity for nitrogen adsorption, depending on the chemical nature of the adsorbent, its preparation, etc. All the nitrogen adsorption isotherms obtained in this work had well defined hysteresis loops closing at $p/p_0 \approx 0.45$ (a rather typical value for nitrogen). Nitrogen adsorption/desorption isotherm for medium grain size samples of the three cores investigated are shown in Figure 6. The following characteristics of the samples can be immediately deduced from Figure 6:

- there are large differences in the amounts adsorbed by the three cores (the ratio MLM-3 : NEGU-17 : Prati State 12 at $p/p_0 = 0.4$ is 1 : 2.56 : 0.29, the BET surface areas are 1.31, 4.06, and 0.36 m^2/g, respectively);

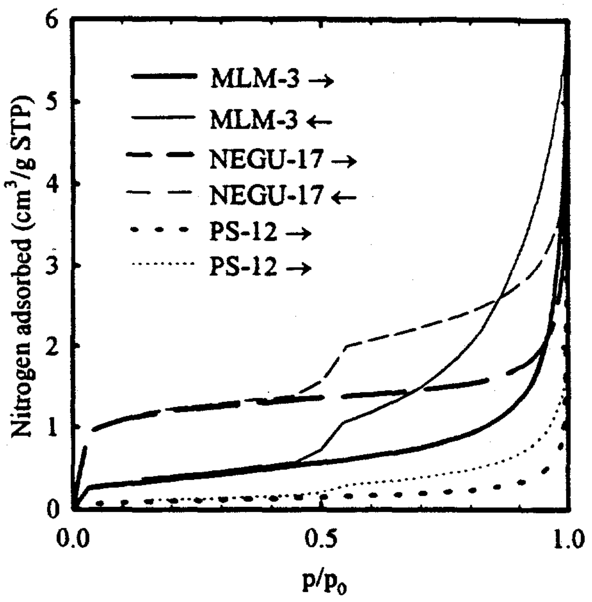

Figure 6. Adsorption/desorption isotherms of nitrogen at 77 K on the medium fractions of the cores of the three wells investigated

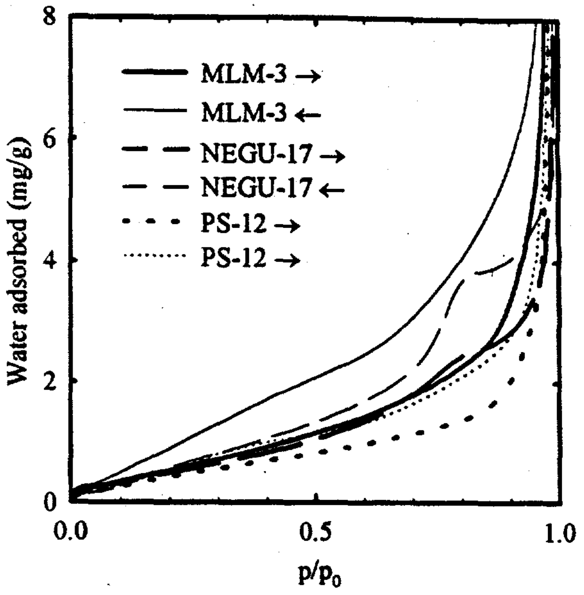

Figure 7. Adsorption/desorption isotherms of water at 200 °C on the average medium and coarse grain size fractions of the cores of the three wells investigated

- the NEGU-17 metagraywacke has the largest specific surface area and its pore area distribution is shifted towards smaller pores compared to the other two cores;
- the MLM-3 metagraywacke has the largest high pressure nitrogen retention, which is likely due to the presence of more macropores.

The relative capacities of various materials for nitrogen adsorption at 77 K cannot be used directly to predict relative capacities for water adsorption, even if the materials are similar. A comparison of Figure 6 with Figure 7, its analogue for high temperature water adsorption, supports this conclusion. Figure 7 shows water adsorption isotherms of the three cores (averages of the medium and coarse fractions) at 200 °C. The following characteristics of water adsorption can be observed:

- the solid-fluid interactions are relatively stronger (as compared to the fluid-fluid interactions) in nitrogen than in water;
- in contrast to nitrogen adsorption, the amounts of water retained by the three cores at low relative pressures are similar (the ratio MLM-3 : NEGU-17 : Prati State 12 at p/p$_0$ = 0.4 is 1 : 0.90 : 0.74;
- the NEGU-17 isotherm has a visibly different shape from the other two isotherms.

There is convincing evidence, obtained by different methods, indicating that the NEGU-17 metagraywacke has not only significantly more micropores but also less very wide macropores than either MLM-3 or Prati State 12. Pore volume distributions were calculated from both nitrogen and water adsorption isotherms. The results were in a very good qualitative agreement, and they both showed a very distinct enhancement of adsorption in the very narrow pore range for NEGU-17 in comparison with the other two cores. Average pore diameters from nitrogen adsorption BET surface areas and total pore volumes for MLM-3, NEGU-17, and Prati State 12 were 272 Å, 66 Å, and 286 Å, respectively. The average pore diameter for NEGU-17 calculated using the Langmuir specific surface area is even lower (47 Å). The pore volume distributions obtained from mercury intrusion tests are shown in Figure 8.

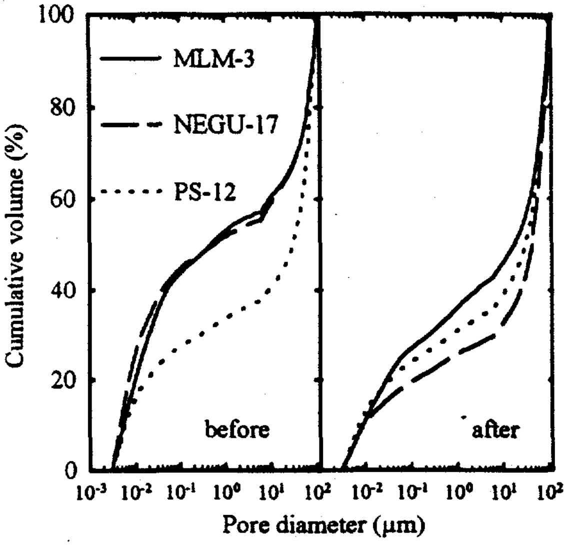

***Figure 8.** Normalized cumulative pore volume distributions obtained from mercury intrusion porosimetry.*

Mercury intrusion can provide information about porous structures in a wider pore size range than nitrogen adsorption, but its precision is lower in the narrow mesopore and micropore ranges. For these reasons the differences between the samples in these ranges are not visible in Figure 8. However, Figure 8 shows a shift towards wider pore sizes which took place during high temperature water adsorption experiments, in NEGU-17 and MLM-3 samples, while Prati State 12 pore volume distribution remained unchanged. Since the smallest pores are most affected by changes occurring on the surface or by solid dissolution and subsequent deposition, the Prati State 12 metagraywacke apparently has by far the smallest amount of very narrow pores. Partial destruction of the finest pores was also indicated by the decrease by 20 to 30 per cent in the BET specific surface areas of all the rock samples investigated after the high temperature water adsorption measurements.

Total pore volumes (and hence total porosities) are difficult to measure unambiguously by either adsorption or mercury intrusion. The adsorption isotherms of rock samples are characterized by a steep increase of the amount of water retained with the increase in pressure towards saturation, so that the isotherm is apparently asymptotic to the $p/p_0=1$ axis. Such behavior is not universal in porous materials, since often a plateau at high relative pressures is found. The lack of a plateau indicates that the pore volume distribution is relatively even in the upper end of the pore size range, and there is no distinct upper pore size limit. Since the widest pores contribute significantly to the total volume (although usually not to the total surface area), this limits the accuracy of total pore volume determinations. The distinction between internal and external volume is arbitrary, and small changes in the relative pressure or mercury filling pressure may introduce large errors. Total porosities obtained in this work from mercury intrusion tests are shown in Figure 9.

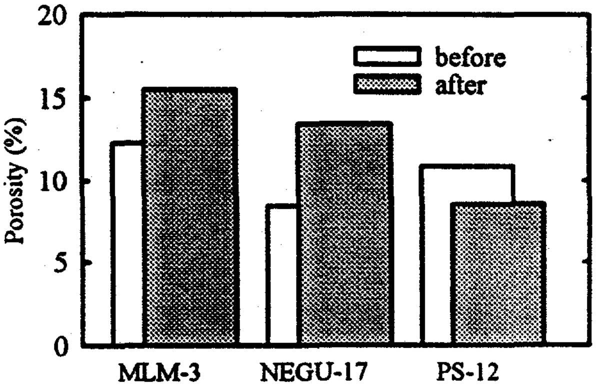

***Figure 9.** Porosities of the samples before (open bars) and after (shaded bars) high temperature water adsorption experiments.*

The porosities were measured by the Micromeritics laboratory using a mercury filling pressure of 1.59 psia, and a final pressure of 60,000 psia. The results are significantly higher than those reported by Satik *et al.* (1996) for similar materials (up to 5.5 per cent for MLM-3 metagraywacke) or by Gunderson (1992) (1.1 to 5.6 per cent for NEGU-17 graywacke). The reason for this discrepancy is not clear. The differences in the mercury intrusion procedures, sample grain sizes, and random differences between the samples can significantly impact total porosity results.

The percentages of the components that account for more than 95 per cent of the metagraywacke are given in Table 1. (Hulen, 1997)

	MLM-3	NEGU-17	PS-12
quartz	38	19	45
albite	30	16	21
chlorite	14	31	13
illite	11	14	4
epidote	1	2	11
adularia	traces	8	3
organic	1	6	2

Table 1. Compositions of the metagraywacke samples.

The compositions shown in Table 1 indicate that the fine NEGU-17 metagraywacke differs significantly from the other two more coarse-grained samples in the relative amounts of quartz, albite, and chlorite. It also contains much more organic matter. The Prati State 12 metagraywacke contains more quartz and epidote but less illite than either NEGU-17 or MLM-3. Chlorite has a layered structure similar to montmorillonite and other minerals forming clays and capable of a reversible uptake of water with swelling and splitting into lamellar structures. Quartz and feldspars have more rigid, three dimensional structures which do not accommodate water or small cations as easily. However, their surfaces can be irreversibly hydroxylated.

CONCLUSIONS

Measurements of adsorption of water on rock samples were made for the first time at the reservoir temperature. The amounts of water retained by samples of three cores taken from The Geysers reservoir as a function of relative pressure of steam at 150 °C, 200 °C, and 250 °C are the principal results of this work. These results support the view that only the amount of water held in the pores as capillary condensate can change significantly with temperature. This means that the amount of water retained by the porous solid on the desorption branch of the hysteresis loop decreases with increasing temperature, and the hysteresis loop narrows. It is estimated that at 250 °C, and at p/p_0 up to 0.9, no more than 20 per cent of the water present in the rocks investigated can be retained by the capillary condensation mechanism (with liquid-gas menisci of small, mesopore scale radii, present). Below $p/p_0 = 0.75$ at this temperature there is practically no temperature-dependent capillary condensation, and adsorption/desorption essentially does not depend on temperature in the range investigated.

Reversible physical adsorption/desorption was observed on all the samples. Both the MLM-3 and Prati State 12 metagraywackes show low pressure hysteresis, but the NEGU-17 does not. The latter rock has the finest structure of the three and shows some microporosity, which, however, does not affect significantly the amounts of water adsorbed.

Irreversible bonding of water occurs on all the samples after they are milled to finer grain sizes (below 0.355 mm). The amount of water retained irreversibly can be many times larger than the capacity for physical adsorption. The fact that only fine grain size fractions show appreciable irreversible water retention indicates that the minerals susceptible to chemical adsorption (or alteration) are initially protected by a material that does not bond water, or has already been altered. The differences in water and nitrogen adsorption find their reflection in the mineral composition of the rocks, but a detailed analysis of the roles played by various component minerals would require further studies.

It is not surprising that the differences in the BET nitrogen adsorption specific surface areas of the samples do not reflect the differences in water adsorption capacity. Since the relative strength of the solid-fluid interaction (compared to the fluid-fluid interaction) is much greater in highly polarizable nitrogen than in the polar and hydrogen bridged water, nitrogen molecules can penetrate some pores that the smaller water molecules can not. As a result, some microporous solids with polar groups may show an enhancement of low-pressure adsorption which is much greater for nitrogen than for water.

Total porosity is difficult to measure accurately and it can not be treated as a reliable measure of water adsorption capacity. Low temperature nitrogen adsorption/desorption results can be useful if the pore volume and area distributions are analyzed and calculated in a uniform way. Since geothermal reservoir rocks show a variety of structures, with various configurations of the pore systems and with composition-dependent reversible chemical adsorption, water retention estimates obtained from such calculations are not expected to be reliable. The best estimates of water retention may be obtained from experiments at ambient or moderately superambient temperatures which can be corrected for the temperature dependence of the capillary condensation.

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