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ADSORPTION CHARACTERISTICS OF ROCKS FROM VAPOR-DOMINATED GEOTHERMAL RESERVOIR AT THE GEYSERS, CA

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ABSTRACT

This paper reports on a continuing experimental effort to characterize the adsorption behavior of rocks from The Geysers steam field in California. We show adsorption results obtained for 36 rock samples. All of the adsorption isotherms plotted on the same graph exhibit an *envelope* of isotherms. The minimum and the maximum values of the slope (or rate of adsorption) and of the magnitude within this *envelope* of isotherms belonged to the UOC-1 (felsite) and NCPA B-5 (serpentine) samples. The values of surface area and porosity, and pore size distribution for 19 of the samples indicated a very weak correlation with adsorption. An interpretation of the pore size distributions and the liquid saturation isotherms suggests that the change in the slope and the magnitude of the adsorption isotherms within the *envelope* is controlled primarily by the physical adsorption mechanism instead of capillary condensation. Grain-size and framework grain to matrix ratio are found to be insufficient to characterize this adsorption behavior. An accurate identification of the mineralogy of the samples will be essential to complete this analysis.

INTRODUCTION

In general, geothermal systems can be categorized as liquid- or vapor-dominated reservoirs depending on liquid water saturation level. In liquid-dominated systems, the resident fluid is mostly hot liquid water while it is mostly saturated or superheated steam in vapor-dominated systems. Vapor-dominated systems are the most attractive commercially because of their high energy content. Examples of such systems are Larderello, Italy and The Geysers, CA. The focus of this study has been on The Geysers geothermal field in California.

In an early attempt to explain the source of The Geysers geothermal reservoir, White (1973) suggested that liquid might either be supplied from an external water aquifer or exist at an adsorbed state in pore space. Since further research has failed to prove any evidence of such an external water source, the phenomena of adsorption is the more likely mechanism. If this is the case, then it is very important to identify and to measure the quantity of so called “adsorbed water” in the reservoir in order to forecast correctly the production capacity and the life of the reservoir. Moreover, the effects of this phenomenon must be accounted for when designing a proper reinjection/production process in The Geysers since both fluid transport and storage will depend on how strong such effects are.

Although the fundamentals of the adsorption phenomena has long been well known and the body of the literature on the subject of adsorption at low temperature is large, the studies regarding adsorption at high temperatures are limited. Previously, a number of experimental and theoretical attempts were made at Stanford in order to measure the amount of adsorbed water and to improve the understanding of the adsorption behavior at The Geysers field. In 1980, Hsieh constructed a *BET* (Brunauer, Emmett and Teller) type of sorptometer and conducted adsorption experiments with Berea sandstone core and unconsolidated silica sand. His results showed that adsorption behavior is affected by temperature and that steam adsorption is a possible water storage mechanism (Hsieh and Ramey, 1983). Later, Luetkehans (1988) improved this equipment and conducted more experiments with Berea sandstone as well as with geothermal rock samples. Due to the excessive leaks that occurred during the long equilibrium times required when using core samples with very low porosity and permeability, the accuracy of these results were questioned. This problem was also encountered by Herkelrath et al. (1983) and Herkelrath and O’Neal (1985) in the studies of steam flow in porous media and nuclear waste disposal. Previous studies indicated the need for a better apparatus that could provide a better control of experimental errors.

After the acquisition of an improved, computer automated, high temperature adsorption equipment, Harr (1991) and Shang at al. (1994a,b) reported a number of preliminary adsorption measurements on tight rock samples. Additional experimental results for the rock samples from The Geysers field were reported recently by Satik and Horne (1995). A comparison of the results obtained at 80, 100 and 120 ^{o}C showed that the effect of temperature is negligible on the adsorption cycle whereas it is of significance during the desorption. The results of Satik and Horne (1995) also revealed another interesting feature. Adsorption behavior for a few samples randomly selected at the various locations in The Geysers showed a possible adsorption *envelope* ranging from a low-valued curvilinear to a large-valued linear type of isotherms. The cause of these changes in the adsorption behavior was unclear. These results indicated the need for further research to understand and to characterize this behavior, which then led us to a more detailed and systematic study. The ultimate goals of this project are to ascertain if a correlation exists between adsorption behavior and intrinsic chemical and physical properties such as mineralogy, permeability and porosity, and to conduct an *adsorption survey* of the Geysers field if such a correlation exists.

In this paper we report the continuing experimental effort towards this final goal. First, we discuss the general geologic condition at The Geysers and describe the main rock types. Next, we shall explain the methodology followed during the process of sample selection. Following this, we give a brief description of the experimental apparatus and procedure. Finally, we discuss the results of the adsorption experiments conducted for The Geysers samples selected for this study.

GEOLOGIC SETTING OF CORES

General Geologic Condition at The Geysers

The Franciscan Assemblage in the vicinity of The Geysers is well-known and described in numerous publications in detail that will not be repeated here (e.g.: Bailey et al., 1964; McLaughlin and Donnelly (editors), 1981; GRC Special Report 17, 1992). At The Geysers, the Franciscan Assemblage occurs as a sequence of tabular, stratigraphically continuous, slabs bounded by thrust faults known to some as "thrust packets" which dip eastward (Thompson, 1992). These were intruded by a composite, shallow, granitic Quaternary pluton of batholithic proportions thought to underlie an area of approximately 40 to 50 square miles beneath The Geysers.

A large portion of The Geysers geothermal reservoir is within a thick, areally extensive body of metamorphic, graywacke sandstone. This body of metagraywacke can be subdivided into turbidite deposits of deep water submarine fans. In the Central portion of The Geysers, the metagraywacke section is often composed of massive, medium to coarse-grained proximal sandstone turbidites. In the Northwest Geysers, the metagraywacke units become thinner and finer grained, with intervals of siltstone and argillite interbeds, and other stratigraphic features characteristic of distal turbidite sequences (Sternfeld, 1989). The metagraywacke reservoir is interrupted by tectonically mixed units of rocks known as "melange" in the Northwest Geysers, and greenstone in the Southeast Geysers. The vast majority of steam entries in Geysers wells, however, occur in metagraywacke.

In the Central and Southeast Geysers, ophiolitic sequences of Franciscan greenstone, chert and serpentinized peridotite are the thrust packets which outcrop and form the caprock to much of reservoir. In portions of the Northwest Geysers. However, metagraywacke both outcrops and forms the entire geothermal reservoir section; the difference being that the metagraywacke "caprock" does not have an open fracture system, and the reservoir graywacke does. In the Northwest Geysers, the metagraywacke section above the pluton is believed to be at least 11,000' thick. In the Southeast Geysers where the pluton is shallowest (now at -500 feet subsea elevation), the overlying metagraywacke section is as thin as 3500' thick. Here, the pluton was intruded sufficiently shallow into the crust so that the fracture system caused by the pluton reached the surface causing venting, decompression, boiling and convection (Walters et al., 1988).

Felsite

The term "felsite" is a general term applied to light-colored igneous rocks, and used locally to designate a large, granitic intrusive complex of batholithic proportions which is known to underlie The Geysers. An extensive study on this pluton has been reported in Hulen and Walters (1994).

The three major rock phases recognized by Hulen and Walters (1994) to underlie the Central and Southeast Geysers are: Hornblende-pyroxene-biotite *granodiorite,* leucocratic biotite microgranite *porphyry* and orthopyroxene-biotite *granite.* The shallowest major felsite phase is rhyolite porphyry. Orthopyroxene-biotite granite dominates the top of the felsite in the Central Geysers. This granite is apparently a high-silica (77%) variety, though its composition has clearly been modified in part by hydrothermal alteration. Apparently the youngest and certainly the most mafic of the three major felsite phases is a distinctive, dark-colored granodiorite occurring at depth in the eastern portion of The Geysers. A core from this intrusive phase contains 67% SiO2; thus it appears chemically to be a true granodiorite.

The intrusion of the felsite may have created both the vertical and horizontal fracture permeability and the basic "plumbing" needed to integrate pre-existing fractures remaining from the Jurassic-Cretacous subduction. Tertiary uplift and Quaternary tectonism of the San Andreas Fault Zone. As discussed by Sternfeld (1989), there is a strong correlation between occurrences of five major steam anomalies delineated by Thomas (1981) and the shallowest occurrences of steam underlain by the shallowest known occurrences of the felsite (Hebein, 1986). Many of the larger wells are also in close proximity to the drilled apices of the felsite.

The Geysers felsite is the basement rock in the Southeast and Central portions of The Geysers geothermal reservoir and is also the probable "basement rock" in the Northwest. More than 60 deep geothermal wells have penetrated the felsite. The overlying metagraywacke is thermally metamorphosed to a distance of 1000' to 2500' by the felsite throughout The Geysers (Walters et al., 1988; Sternfeld, 1989). The drilling data indicate that the thickness of The Geysers felsite may exceed 10,000 feet.

Metagraywacke

The reservoir rock at The Geysers is often called "graywacke", or the "main graywacke"; however this name belies the fact that the reservoir rock is primarily metagraywacke and has lost the petrophysical values associated with sedimentary sandstone. Previous analysis of cores from The Geysers reservoir show that the graywacke sandstone and intercalated shale have been metamorphosed to metagraywacke and argillite; that intergranular porosity has been reduced to almost nil; and that measurable porosity and permeability is in microfractures, along welded grain contacts, and in dissolution pores.

The Geysers "graywacke" is, in fact, a pumpellyite-grade metagraywacke with a weak and localized textural fabric (Type 1+) described by Blake et al. (1967), and McLaughlin (1981). Although the textural and mineralogic grade of the metagraywacke is "weak" by petrographic standards, the metamorphism has had a significant effect on the porosity and permeability of the original graywacke sandstone. The Geysers "graywacke" should be classified as metagraywacke for petrophysical purposes after the usage of Hulen et al. (1991) when discussing its reservoir properties.

Graywacke is a subclass of sandstone. It consists of sand grains of quartz, feldspar and rock fragments embedded in a well-indurated dark gray to black clayey matrix. Matrix percentages greater than 15% are common and often exceed 50% of the total rock. Graywacke is composed of two components: framework grains and matrix material interstitial to the framework grains.

Framework grains range widely in size, from pebble to sand to silt particles (64mm to 0.01mm), and in composition. They are primarily quartz and feldspar with trace to minor accessory minerals such as epidote and biotite. Polymineralic rock fragments include greenstone, argillite, and chert. Most detrital grains are subangular to subrounded in shape.

Graywacke matrix is not a homogeneous monomineralic cement. It is an extremely inhomogeneous paste composed of many constituents. The most common are: silt-sized framework grains; incompetent lithic fragments such as greenstone which have been crushed and squeezed between competent framework grains; silica cement; and phyllosililcates cements including illite, montmorillonite, sericite and chlorite.

A fundamental aspect of the framework grain to matrix ratio is that the proportion of the matrix material increases as the size of the framework grains decreases. Thus, fine to very fine graywackes will appear more argillaceous because greater than 50% of the rock may be composed of matrix paste. Coarse-grained graywackes, characterized by matrix percentages of less than 20% will appear to be cherty or siliceous. In actuality, the matrix paste is an admixture of clay cement and silica cement. It has a siliceous appearance because both silica and crystalline clay minerals are colorless at high magnification under a microscope. When the matrix material is primarily argillaceous, and the grains range from 0.01 to 0.05 mm, the rock is classified as argillite. Argillite is therefore an "end member" of the metagraywacke-argillite facies, as shale is an "end member" of the sandstone-shale facies.

METHODOLOGY

Sample Selection

The Geysers reservoir is a 1000 m to 3500 m thick section of Mesozoic metagrawacke with an area of about 75 sqkm which has been intruded by a Quaternary granitic body of batholithic proportions locally known as "the felsite". More than 85% of the reservoir volume and steam resource are in the metagraywacke and granitic intrusive rocks, the remainder of the reservoir volume being intercalated units of metashale ("argillite"), metavolcanic greenstone, and serpentinite which have been tectonically mixed with the metagraywacke. The metagraywacke is derived from proximal and distal turbidite units which range from dark, fine-grained, argillaceous rock to light gray, coarse-grained litharenites. The essential difference between the metagraywacke subtypes is the grain size, and the amount of matrix paste which includes sericite (illite), chlorite, and smectite. A correlation between these lithologic differences in the metagraywacke the adsorption behavior is sought.

36 samples of core at 18 locations in the vapor-dominated reservoir at The Geysers were selected for adsorption measurements. These samples were selected to represent the variations in lithology across the reservoir so that the measurements can be used to define the adsorption properties of each significant rock type, and to determine if correlations with adsorption can be made with depth, geologic structure, and other physical properties including porosity, surface area, and pore structure.

Distribution of the samples selected for this study were as follows: thirteen silty to fine-grained, twelve medium-grained and five medium to coarse-grained, lithic metagraywacke samples of core were selected within metagraywacke. There are three units known within the felsite intrusive complex: a biotite granite being areally most extensive at the top of the pluton; a granodiorite apparently predominant at depth, having assimilated the biotite granite; and a rhyolite porphyry. One sample from each of these three felsite units were selected. Argillite is an end member of the graywacke-argillite facies in the same manner as shale is an end member of the sandstone-shale facies. One argillite sample of core was selected. Finally one sample of greenstone and one sample of serpentine were also included. The Geysers steam field is elongated along a NW-SE axis. The geographic distribution of the 36 samples is weighted toward the center of the field where the large number of wells are drilled: nine samples from Northwest Geysers, 19 samples from Central Geysers and eight samples from Southeast Geysers.

Experimental Apparatus and Procedure

Our experimental apparatus is a computer-automated, high temperature sorptometer (built by Porous Materials, Inc.). Details of the experimental apparatus and procedure were given in Satik and Horne (1995). Briefly, 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. 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 (currently up to 150 °C). 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. A control software loaded in the computer system is used to operate and carry out sorption experiments.

Since the equipment is computer-automated, the experimental procedure is simple. Normally, an operator only needs to load the sample and start the control software. The remaining experimental procedure is carried out under computer control. Before each experiment, a new sample is outgassed under vacuum for 10-12 hrs. at 180 °C. Then, the procedure summarized in Satik and Horne (1995) is followed to obtain points on an adsorption or a desorption isotherm.

Due to the physical configuration of the sample cell (a steel U-tube with inner diameter of 9.65 mm), before starting each experiment, the rock (core) samples to be used are normally crushed into smaller pieces (particle size of 0.355 mm or larger). This procedure raises an important question regarding the sensitivity of the results to the particle sizes. Therefore, in order to address this point adsorption experiments have been carried out with crushed rock samples sieved at four different mesh ranges (particle sizes of up to 2 mm, 0.833-2 mm, 0.355-0.833 mm and 0.104-0.355mm). The adsorption curves obtained for the samples with particles of sizes of 0.355 or larger are similar while it differs significantly when the particle size are between 0.104

and 0.355 mm (Figure 1). These results suggest that the use of crushed samples that contain particles of at least 0.355 mm large is appropriate to represent the overall adsorption behavior. Moreover, the adsorption equilibrium time could be extremely long for tight core samples, such as from The Geysers, with porosities of order of a few percent. Use of moderately crushed samples conveniently reduces the experiment run time and reduces the danger of leaks.

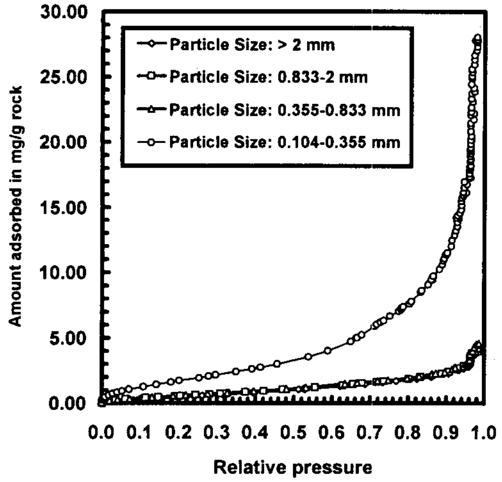

Figure1. The effect of particle size on adsorption.

DISCUSSION OF RESULTS

Sorption experiments were carried out towards the final goal of conducting an *adsorption survey* of The Geysers geothermal field. 36 samples were selected by following the methodology outlined above. Although both adsorption and desorption isotherms have been obtained experimentally at 120 °*C* for all of The Geysers samples selected, we discuss only the adsorption isotherms in the scope of this paper. Analysis of the desorption isotherms will be given in a future paper.

After the adsorption experiments were completed for all of the samples, measurements of surface area, porosity, pore size distribution and grain density were also performed on the same samples at a commercial laboratory. A summary of all of the results are given in Table 1. All of the sorption data obtained in our laboratory are currently accessible to the public through the Internet. Our World Wide Web page URL address is: http://ekofisk.stanford.edu/geoth/ads-data.html.

Table 1: Summary of the results

In Figure 2, the adsorption isotherms obtained from the sorption experiments for all of the 36 samples selected for this study are shown. The figure shows an *envelope* created by the end-point isotherms of UOC-1 and NCPA B-5 samples. The slope and the magnitude of these isotherms within the *envelope* is the largest for NCPA B-5 and the smallest for UOC-1 while all of the other isotherms fall within these two curves. NCPA B-5 is the only core sample of serpentine and its lithologic description (Table 1) is serpentine, serpenitized very fine-grained metagraywacke and silty-textured argillite, all of which are expected to have a very strong adsorptive behavior. On the other hand, UOC-1, leucocratic rhyolite porphyry (high silica granite), is one of the three felsite samples selected for this study.

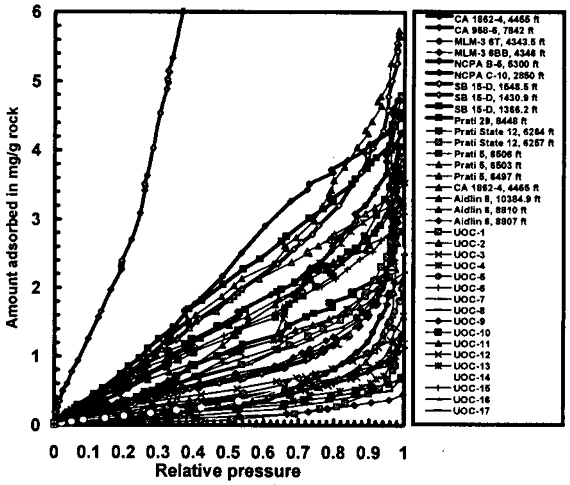

Figure 2. Results of the adsorption experiments for the 36 Geysers samples.

CORE	Elev. to Steam from Core, ft	Elev. to Felsite from Core, ft	ROCK TYPE	ADSORPTION at P/Po=0.5, mg/g	ADSORPTION at P/Po=0.75, mg/g	ADSORPTION, Langmuir Coef, c	ADSORPTION, Langmuir Coef, d	SURRFACE AREA, m^2/g	POROSITY VOL. %	DENSITY G/CM3	LITHOLOGIC DESCRIPTION
AIDLIN 6	139	unknown	medium mgw	0.443442758	1.038067799	0.165176903	3.124115375	0.6704	3.33	2.7029	Med. gray, medium-grained, massive mgw
AIDLIN 6	142	unknown	medium mgw	0.125196726	0.350883131	0.030980009	4.103252109	0.39	5.03	2.736	Med. gray, medium-grained, massive mgw
AIDLIN 8	710	unknown	argillite	1.74369027	3.225969482	0.450203339	5.613147248	0.0709	2.28	2.8008	Dk. gray argillite
CA1862-4	-75	-3000	fine mgw	2.176996406	3.405932502	0.847721503	4.743964583	0.5374	3.26	2.8093	Dark gray, fine grained, gneissic metagraywacke
CA1862-4	-65	-3000	coarse mgw	1.242854467	2.093908941	0.642154185	3.17718897	0.3158	2.62	2.766	Dark gray, predominantly coarse grained, sl. foliated mgw.
CA958-6	2171	52	felsite	0.187645997	0.510575498	0.043602634	4.403777051	0.1339	3.59	2.7395	Dark, hornblende-pyroxene-biotite granodiorite.
MLM-3	-1735	-4270	fine mgw	0.287612052	0.769594919	0.062346583	4.817630776	0.7551	5.52	2.7507	Med. light gray, fine to medium grained metagraywacke
MLM-3	-1733	-4268	medium mgw	0.375962782	0.960486522	0.093051579	4.374406985	0.874	5.11	2.7466	Med. gray, med. grained metagraywacke.
NCPA B-5	500	-2600	serp.&serp. mgw	7.781898089	11.78075987	0.96399811	15.85415954	1.8689	5.74	2.8816	Serpentine & serpenitized v.f.-grained mgw and silty- textured argillite
NCPA C10	273	-4495	greenstone	1.378674198	2.4821875	0.500138242	4.135059559	0.9177	3.42	3.0126	Med. to dark green, hard, aphanitic greenstone.
P. S. 12	1479	-3700	fine mgw	0.955847335	1.670237934	0.555723471	2.670894211	0.7905	4.17	2.7616	Med. gray, fine grained metagraywacke
P. S. 12	1486	-3700	medium mgw	1.748698582	2.645198841	0.967043897	3.556955812	1.0626	4.49	2.7647	Med. greenish gray, medium grained metagraywacke.
PRATI 29	376	-3500	fine mgw	1.340453565	2.341782735	0.55981203	3.734000321	0.1554	2.65	2.7628	Dark gray, v.fine to fine grained metagraywacke.
PRATI 5	-438	-3500	fine mgw	1.503308544	2.368022468	0.823786149	3.32605298	0.8689	2.67	2.7544	Greenish black, very fine to fine grained metagraywacke.
PRATI 5	-432	-3500	fine mgw	0.525379192	1.215671264	0.164087756	3.671338731	1.46	2.87	2.7461	Med. greenish gray, fine to medium grained metagraywacke.
PRATI 5	-429	-3500	medium mgw	1.071462876	2.137912778	0.330153823	4.29616985	0.9862	3.04	2.7586	Med. dark gray, medium grained metagraywacke.
SB-15	-3	-3700	medium mgw	2.024311896	3.165671185	0.848605643	4.408681551	1.333	2.74	2.7473	Med. dark gray, medium grained, metagraywacke.
SB-15	62	-3700	fine mgw	1.5823974	2.984396318	0.414130715	5.385491689	3.1634	6.19	2.7346	Med. dark gray, fine grained, thin-bedded metagraywacke.
SB-15	179	-3500	coarse mgw	0.499556193	1.063516471	0.252433222	2.467831031	1.9125	3.59	2.7426	Med. gray, medium to coarse grained metagraywacke.
UOC-1	-587	435	felsite	0.07222295	0.195479	0.058568577	1.296102026				Leucocratic rhyolite porphyry (high-silica granite).
UOC-10	1549	-413	medium mgw	0.225531665	0.400805373	0.518354001	0.656901708				Med. lt. gray, medium grained metagraywacke.
UOC-11	1597	-3200	coarse mgw	1.076441945	1.54456015	1.201262936	1.973286566				Brownish gray, med.and med. to coarse grained lithic metagraywacke
UOC-12	1598	-3200	medium mgw	0.439153643	0.803996494	0.462512973	1.383283705				Lt. olive gray, medium grained metagraywacke
UOC-13	1601	-3200	fine mgw	1.112390192	2.082383431	0.429710264	3.695941755				Med. dark gray to brownish gray, fine grained mgw and metasiltstone
UOC-14	4560	1790	felsite	0.360572497	0.848939613	0.151280489	2.712817106				Orthophyroxene-biotite granite
UOC-15	678	-3137	fine mgw	1.335623304	2.098352712	0.833887208	2.936713927				Med. dark gray, fine to medium grained metagraywacke
UOC-16	686	-3129	fine mgw	0.78016668	1.34139546	0.593910362	2.093313588				Medium gray, fine grained metagraywacke
UOC-17	694	-3121	fine mgw	0.855964644	1.499180269	0.554071852	2.399520923				Med. gray, fine grained and dark gray v. fine grained metagraywacke
UOC-2	404	-2356	coarse mgw	0.350154005	0.659013619	0.407128002	1.196950307				Lt. to med.-lt. gray, med. to coarse grained metagraywacke
UOC-3	406	-2354	medium mgw	0.27368017	0.555552304	0.307956462	1.153453239				Lt. gray, medium grained metagraywacke
UOC-4	409	-2351	medium mgw	0.163969015	0.386676252	0.157435073	1.190794487				Lt. to med.-lt. gray, fine to medium grained metagraywacke
UOC-5	95	-1019	fine mgw	0.324665534	0.719791718	0.20836002	1.853467844				Dark gray to dk. greenish gray, v.fine grained metagraywacke.
UOC-6	97	-1017	coarse mgw	0.296036205	0.575503623	0.369636055	1.090154362				Light gray, coarse grained metagraywacke
UOC-7	99	-1015	medium mgw	0.359945996	0.637166946	0.516164962	1.048291888				Med. light gray, medium grained metagraywacke
UOC-8	1544	-418	medium mgw	0.166974857	0.328268873	0.351924842	0.637668515				Med. light gray, medium grained metagraywacke
UOC-9	1547	-415	fine mgw	0.115377768	0.224802036	0.362073405	0.430718122				Brn. black metasiltstone and grn. gray, fine to med. grained mgw

The adsorption isotherms given in Figure 2 include contributions from both surface (physical) adsorption and capillary condensation mechanisms of the adsorption phenomena. To analyze these results, some information about the contributions of each of the two mechanisms to the total amount adsorbed is needed. The first mechanism is related to the chemical and/or mineralogic composition of the rock while the second is mainly controlled by the topology of the rock (porosity, pore size distribution etc.). Shown in Figure 3 are the volumetric fraction vs. pore diameter value curves for 19 samples, excluding all of the samples (surface area and porosity measurements on the samples are pending). These results were obtained from the equilibrated-step mercury intrusion experiments conducted at a commercial laboratory. In Figure 3, the volumetric fraction denotes the ratio of the total mercury injected (in volume) at a pore diameter step to the total cumulative mercury injected (in volume) at the smallest pore diameter. The total cumulative volume of mercury injected at the smallest pore diameter is also the total pore volume within the rock detected by this method. The smallest value of the pore diameter obtained from these experiments is about 0.003 micrometer which requires a mercury pressure of as high as 60,000 psia.

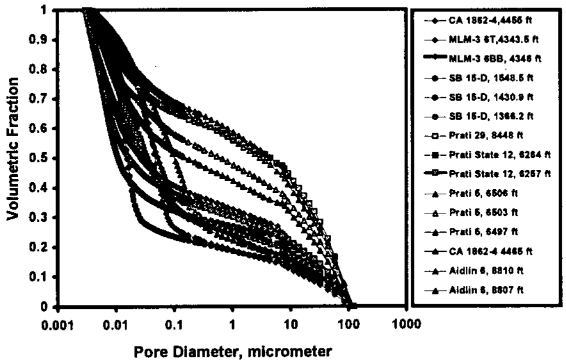

Figure 3. Pore size distributions for the 19 Geysers samples obtained from the mercury intrusion experiments.

In order to have a direct comparison, the rock samples used for adsorption measurements were also used for the mercury injection experiments. As discussed above, all of these rock samples were previously broken into smaller pieces (gravel-sized) before the adsorption experiments were conducted. However, we must note that the breaking process must have increased the external surface area, which in turn has increased the accessibility of pore space. Therefore, the total pore volume and the porosity values (see Table 1) obtained from the mercury injection experiments should represent the absolute rather than the effective values. The effective values are expected to be somewhat smaller. Results shown in Figures 2 and 3 are consistent. An *envelope* similar to that in Figure 2 is also apparent in Figure 3. Figure 3 shows that the lowest- and highest-end curves of the *envelope* belong to the samples from Sulphur Bank 15-D (1430.9 ft) and Prati 5 (6497 ft), respectively. The lowest-end curve reads a pore volume distribution as follows: 70% by the pores of sizes of 0.025 micrometer or less, 15% between 0.025 and 7 micrometer and 15% by the pores of sizes of 7 micrometer or larger. On the other hand, the pore volume distribution for the highest-end curve is as follows: 21% by the pores of sizes of 0.025 micrometer or less, 32% between 0.025 and 7 micrometer and 47% by the pores of sizes of 7 micrometer or large.

In Figure 4, we show the liquid saturation vs. relative pressure curves obtained by using the adsorption isotherms given in Figure 2 and the total pore volume values obtained from the mercury injection experiments. From the figure, the final saturation values at the end of the adsorption cycle for Aidlin 6 (8810 ft) and NCPA B-5 (5300 ft are 0.147 (at p/p_o =0.98) and 0.662 (at p/p_o =0.995), respectively. The capillary condensation mechanism in pores are traditionally described by Kelvin's equation. Simply, this equation provides a relationship between a relative pressure and a characteristic radius (called Kelvin radius). At any capillary condensation stage, steam phase existing in all pores with a radius smaller than the Kelvin radius will be condensed through the capillary condensation mechanism. (Satik and Yortsos, 1995). For typical geothermal conditions, one can calculate a Kelvin radius value of 0.003 micrometer at p/p_o=0.91. The radius value of 0.003 micrometer is selected because it is the smallest pore radius detected by mercury injection experiments. At p/p_o=0.91, the liquid saturation values for the samples from Aidlin 6 (8810 ft) and NCPA B-5 (5300 ft) are 0.05 and 0.6, respectively (Figure 4). Therefore, adsorption process until at p/p_o=0.91 must take place only through the physical adsorption mechanism since the capillary condensation mechanism simply could not have started by the Kelvin equation. Interestingly enough, at this relative pressure value, %34 of the total adsorption has already taken place for Aidlin 6 (8810 ft) and %91 for NCPA B-5 (5300 ft). Therefore, we conclude that the rate of adsorption (the slope) for the isotherms shown in Figures 2 and 4 must be controlled only by the surface adsorption mechanism which depends mostly on the chemical/mineralogic composition of the rock.

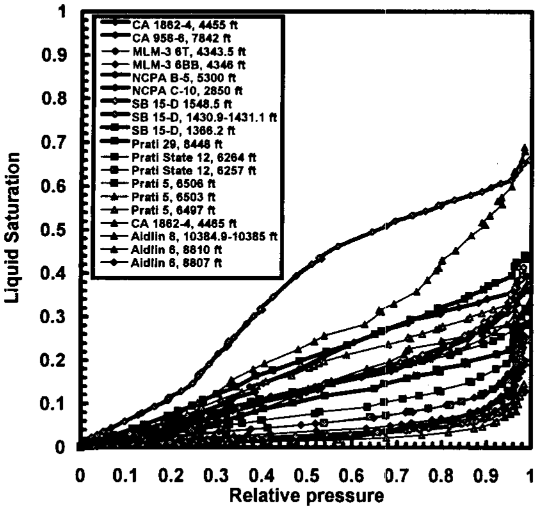

Figure 4. Liquid saturation vs. relative pressure curves obtained for the 19 Geysers samples.

Figure 5 shows adsorption isotherms normalized with surface area values for the 19 Geysers samples. An *envelope* similar to that in Figure 2 is also obtained which suggests that these changes observed in the adsorption behavior (the slope and the maximum adsorption value) are not caused by the surface area. However, surface area values for the remaining samples (for which measurements are still in progress) are required to fill in this *envelope.*

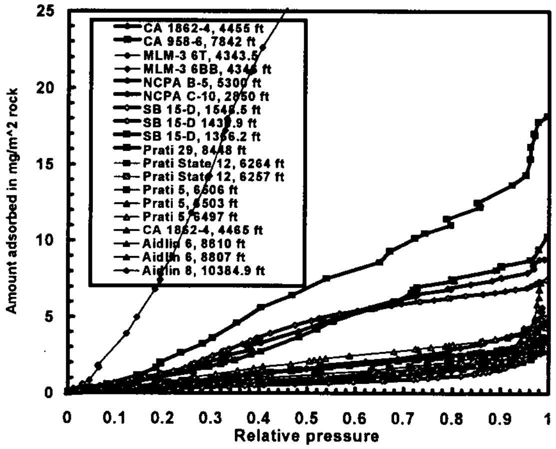

Figure 5. Surface area normalized adsorption isotherms for The Geysers samples.

Figures 6, 7 and 8 show the adsorption isotherms obtained for the samples of fine grained-, medium grained- and coarse grained-metagraywacke subunits, respectively. A similar *envelope* with a large variation is seen also within the each subgroup of metagraywacke. The rate of adsorption (slope of isotherm) and the maximum adsorption value are expected to be higher for the fine to very

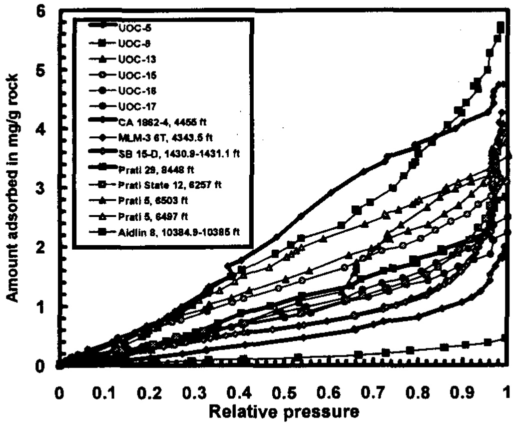

Figure 6. Adsorption isotherms for all of the fine grained-metagraywacke Geysers samples.

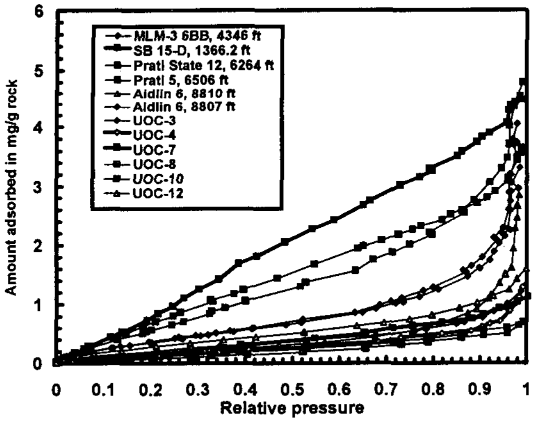

Figure 7. Adsorption isotherms for all of the medium grained-metagraywacke Geysers samples.

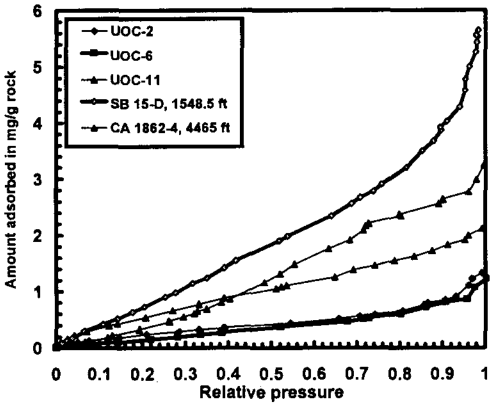

Figure 8. Adsorption isotherms for all of the coarse grained-metagraywacke Geysers samples.

fine grained-metagraywacke than for the medium or coarser grained-metagraywacke due to the fact that coarser samples have more grain than matrix material, therefore, they may contain less highly adsorptive minerals within the matrix. However, a comparison of the isotherms for the samples within the same subgroup shows that the grain size is apparently not a primary factor causing these changes. On the other hand, we believe that mineralogy may still be a key factor because samples from the different subunits of metagraywacke may actually have comparable amounts of highly adsorptive minerals (clays, micas etc.) although their matrix-grain ratio values are quite different from each other. Some of the most adsorptive metagraywacke samples in each subgroup are from the caprock, or near the top of the reservoir, SB 15-D is an example, and work by Hulen and Nielson (1995) shows that mixed-layer illite/smectite is a common vein mineral. This issue can be resolved by identifying the mineral contents for each Geysers sample and may be achieved by X-ray diffraction and/or thin-section analysis methods both of which are currently under consideration.

In Figure 9, we show the adsorption isotherms obtained from the experiments for the three felsite samples selected from The Geysers. Although we had only three samples from the felsite, these isotherms seem to agree well with each other and show an adsorption behavior similar to silicic metagraywacke. The felsite is predominantly plagioclase and quartz with relatively less mica/clay minerals (having a smaller rate of adsorption). However, considering the number of the felsite samples used, the agreement might well be coincidental. More adsorption experiments from the felsite are required to justify this.

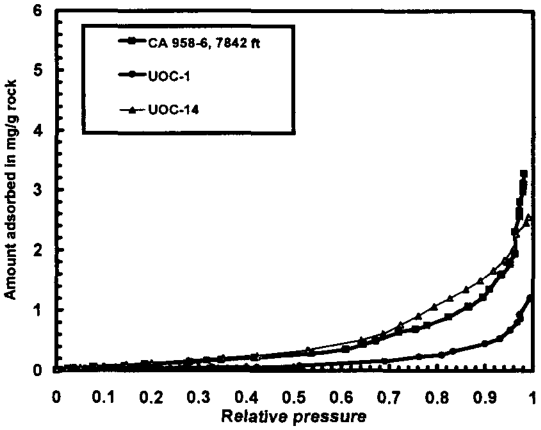

Figure 9. Adsorption isotherms for all of the felsite Geysers samples.

Finally, Figure 10 compares the adsorption isotherms for the samples from different rock types,

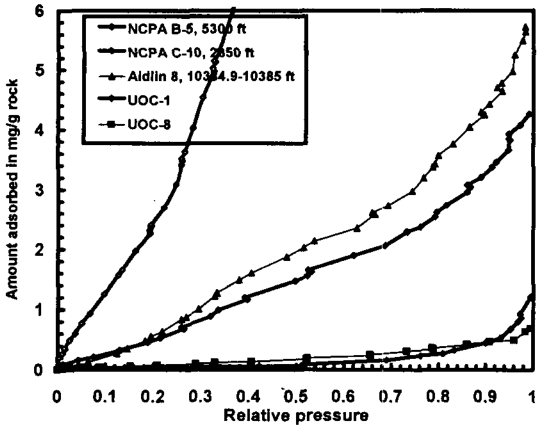

Figure 10. Adsorption isotherms for the samples representing each rock type in The Geysers. The rock types of serpentinite, argillite, greenstone, medium grained-metagraywacke and felsite are represented by the samples from NCPA B-5, Aidlin 8, NCPA C-10, UOC-8 and UOC-1, respectively.

namely serpentinite (NCPA B-5), argillite (Aidlin 8), greenstone (NCPA C-10), medium grained-metagraywacke (UOC-8) and felsite (UOC-1). As expected, the results show that the felsite (UOC-1) and serpentine (NCPA B-5) samples demonstrate the least and the strongest adsorption behavior, respectively, while the greenstone (NCPA C-10) and argillite (Aidlin 8) isotherms fall between them.

The total amount of water stored, and the rates of steam adsorption and condensation vary between the rock types and the subunits of the metagraywacke. Serpentinite appears to be the most adsorptive rock type and granitic felsite may be the least, with an order of magnitude difference between the two. The shapes of some adsorption curves together with mercury injection data suggest a bimodal porosity structure may exist in the metagraywacke.

Argillite and fine-grained metagraywacke have higher rates of adsorption for given pressures, and store several times the amount of water of the coarser grained metagraywacke and granitic felsite. The northwestern portion of The Geysers reservoir is characterized by thick sequences of distal turbidite units consisting of argillite and fine-grained metagraywacke. Consequently, the reservoir rocks of the Northwestern portion of The Geysers reservoir store more adsorbed water than the Central and Southeastern Geysers which is dominated by proximal turbidites units consisting of medium and coarse grained metagraywacke, and granitic felsite.

Greenstone and serpentinite constitute a small but significant portion of the reservoir section in the southeastern Geysers. Although the adsorption properties of the greenstone do not significantly differ from metagraywacke of the proximal turbidite units, the serpentinite found in some melange units is much more adsorptive. Consequently the lithologic details of any particular Geysers well may be important in characterizing the overall adsorptive properties of a particular portion of the reservoir.

CONCLUDING REMARKS

In this paper, we have reported the results of adsorption experiments conducted for 36 Geysers samples. The adsorption results obtained for all of the samples exhibited an *envelope* of isotherms. The minimum and the maximum slope (or rate of adsorption) and absolute adsorption (the largest value attained) values within this *envelope* belonged to the isotherms of UOC-1 (felsite) and NCPA B-5 (serpentine) samples. Surface area, porosity and pore size distribution values for the 19 Geysers samples were measured at a commercial laboratory. Each of these measured values indicated only a very weak correlation with adsorption. Based on the pore size distributions and the liquid saturation isotherms, it was concluded that the change in the slope and the magnitude of the adsorption isotherms within the *envelope* is primarily controlled by the physical adsorption mechanism instead of capillary condensation. The adsorption isotherms for the metagraywacke samples indicate that the grain-size and framework grain to matrix ratio are insufficient measures to characterize this adsorption behavior. A more accurate identification of the adsorptive minerals is needed to complete the interpretation of the experimental results.

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