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A PORE NETWORK MODEL FOR ADSORPTION IN POROUS MEDIA

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ABSTRACT

Using a pore network model to represent porous media we investigate adsorption-desorption processes over the entire range of the relative pressure, highlighting in particular capillary condensation. The model incorporates recent advances from density functional theory for adsorption-desorption in narrow pores (of order as low as 1 *nm*), which improve upon the traditional multi-layer adsorption and Kelvin's equation for phase change and provide for the dependence of the critical pore size on temperature. The limited accessibility of the pore network gives rise to hysteresis in the adsorption-desorption cycle. This is due to the blocking of larger pores, where adsorbed liquid is allowed to but cannot desorb, by smaller pores containing liquid that may not desorb. By allowing for the existence of supercritical liquid in pores in the *nm* range, it is found that the hysteresis area increases with an increase in temperature, in agreement with experiments of water adsorption-desorption in rock samples from The Geysers. It is also found that the hysteresis increases if the porous medium is represented as a fractured (dual porosity) system. The paper finds applications to general adsorption-desorption problems but it is illustrated here for geothermal applications in The Geysers.

INTRODUCTION

In sorption experiments, a condensible gas is introduced into a porous medium, which is initially evacuated. The gas pressure is then progressively increased at constant temperature until it reaches the saturation pressure value at the given temperature. Measuring the amount adsorbed at equilibrium as a function of the relative pressure constitutes the adsorption stage. Desorption is the reverse cycle, where the adsorbed phase desorbs by progressively decreasing the gas pressure. Information on the surface area, the pore size distribution and other properties can be obtained from an analysis of these cycles. Gas adsorption-desorption in porous media differs from adsorption on open surfaces due to two factors, the existence of curved surfaces or pores, where capillary condensation may occur, and possible accessibility or topological effects incurred by the porous medium.

In adsorption of gases over an unconstrained surface, at the early adsorption stage, corresponding to sufficiently small gas pressure, gas molecules are physically adsorbed on the solid surface owing to sorbent-solid molecular interactions. As the process continues, one and subsequently multiple layers of adsorbed fluid cover the solid surface. For larger values of pressure, the thickness of the adsorbed layer is sufficiently large so that the adsorbed fluid behaves as a continuum *liquid* film, at which point a distinct vapor-liquid interface exists. The thickness of the adsorbed layer depends on the gas pressure as well as other parameters that are gas and solid specific. Eventually, as the pressure approaches the saturation pressure, bulk condensation occurs.

In adsorption of gases in pores, the early part of adsorption is similar to the above. Because of the pore wall curvature, however, bulk condensation occurs earlier (at a lower relative pressure) than over a flat surface. This capillary condensation is described by Kelvin's equation, to be discussed in detail below. Additionally, in narrow pores (of the order of a few *nm*), due to the proximity of solid surfaces, the growing film is subject to strong intermolecular forces. As a result, capillary condensation may occur earlier and at conditions different than predicted by Kelvin's equation. For sufficiently small pores, a phase change may actually not occur, and the fluid remains in a supercritical state, as discussed below.

LITERATURE REVIEW

Understanding adsorption-desorption in porous media requires first its understanding in single pores (slits, cylinders), and subsequently the understanding of the collective behavior of an ensemble (network) of pores. Below we briefly review the relevant literature in these two areas.

1. Single-pore models: The literature in this area can in turn be divided into two parts: (i) Surface (physical) adsorption in the absence of pores, where single- and multi-layer adsorption are emphasized. Clearly, no hysteresis in adsorption-desorption cycles is observed here. A comprehensive review of this subject can be found in Gregg and Sing (1982) and Adamson (1990). For the purposes of this paper we note that the thickness of the adsorbed layer can be expressed by various models, of which we shall make use of the following

$$t = \left(\frac{\epsilon_o}{RT \ln \frac{P_{V0}}{P_V}} \right)^{\frac{1}{\alpha}} \tag{1}$$

where t is the thickness of the adsorbed layer, ϵ_o is the adsorption potential of the solid surface, $\frac{P_V}{P_{V0}}$ is the relative pressure, and α is an empirical parameter. This expression is derived from the Frankel-Halsey-Hill (*FHH*) equation [1]. Although used over the entire pressure range, the accuracy of the above equation is questionable at very small pressures. However, for the purposes of this study, we shall use the *FHH* equation over the entire pressure range.

(ii) Adsorption-desorption in pores. Following multi-layer adsorption, capillary condensation occurs. This is traditionally described by Kelvin's equation

$$\ln\left(\frac{P_V}{P_{V0}}\right) = -\frac{2\sigma V_L}{R_g T (R - t)}, \tag{2}$$

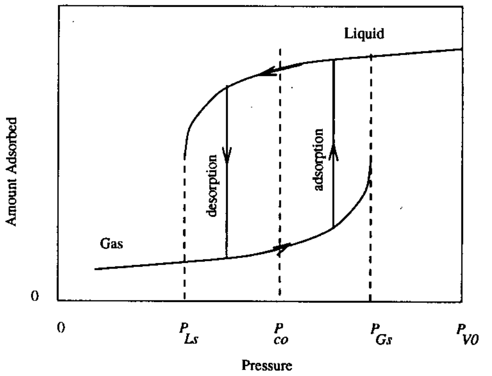


Figure 1: Schematic isotherms indicating single-pore hysteresis (from Liu et al. (1993)).

where $\sigma, V_L, R_g, T, P_V, P_{V0}$ and R are the surface tension, the liquid molar volume, the gas constant, the absolute temperature, the gas pressure, the saturation vapor pressure and the pore radius, respectively. Actually, the above is a modified form of Kelvin's equation, where the pore radius was appropriately reduced by the amount of the adsorbed film. In the standard approach, the onset of capillary condensation denotes an instability of the film (gas-liquid) interface due to the pore curvature. In fact, this mechanism is also responsible for a single-pore hysteresis, where the phase change (from liquid to vapor) during desorption occurs at a radius smaller by a factor of 2 than (2).

An explanation of single-pore hysteresis is given in Figure 1 which shows schematic isotherms for a single pore (from Liu et al. (1993)). Condensation or evaporation in a single pore is to take place at a pressure, P_{co}, at which liquid and gas coexist and the chemical potentials for liquid and gas phase are the same. However, it is possible for condensation and evaporation to be delayed until pressure values different than P_{co}. Now, adsorption and desorption follow the spinoidal branches shown in Figure 1. The onset of phase change may occur at pressure values between P_{co} and P_{Gs} (the spinoidal pressure for the gas phase), and between P_{co} and P_{Ls} (the spinoidal pressure for liquid phase) for condensation and evaporation, respectively. Kelvin's equation in the two different geometries accounts for these two different presures. The end result is that even for a single pore different paths can be followed depending on the direction (condensation or evaporation).

When the pores involved are narrow, fluid

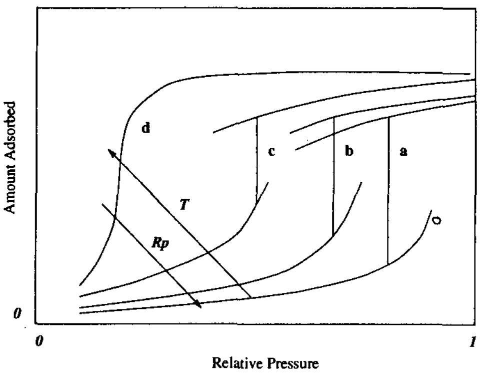


Figure 2: Schematic of adsorption-desorption isotherms in a narrow pore.

molecules interact with solid surfaces on either side of the pore (Evans et al. (1986) and Ball and Evans (1989)), thus adsorption and desorption are strongly affected. Consider, for example, the process in a narrow pore (Figure 2). As pressure increases, the usual adsorption behavior is followed. At low temperatures (and large radius values) the single-pore behavior is as shown in Figure 1. However, as the temperature increases (or the pore radius decreases), the isotherms shift towards the left, while the jumps between liquid and gas branches at the phase transition become smaller (curves a, b and c in Figure 2). Significantly, for a critical value of temperature or a critical size of the pore, the adsorbed fluid becomes supercritical and a clear transition is not observed (curve d in the Figure). Evans et al. (1986) defined this as the *capillary critical point*, beyond which a distinct vapor-liquid interface ceases to exist and the density increases monotonically over the whole range of pressure. Evidently, use of Kelvin's equation will be inappropriate in this range. We note that this behavior is reminiscent of the critical behavior in a bulk liquid. Evans et al. (1986) used a functional density approach to study the characteristics of adsorption in such pores. They obtained the following approximate expression for the critical capillary radius

$$R_{cr} \sim \frac{1}{\lambda}\frac{T_{cr}}{T_{cr}-T} \qquad (3)$$

where R_{cr}, λ and T_{cr} are the critical capillary radius, the decay length of solid-fluid potentials (a function of solid and liquid) and the critical temperature of the fluid, respectively. It should be noted that single-pore hysteresis is also predicted from the theory of Evans et al. (1986), as can be seen schematically in the Figure isotherms.

Along similar lines, but using Monte-Carlo computer simulations, adsorption in narrow pores was studied by Nicholson (1975), Seaton et al. (1989), Aukett et al. (1992) and Lastoskie et al. (1993).

2. Multiple-pore models: Early work on adsorption-desorption made use of the simple model of parallel capillaries (Everett and Haynes (1972)). Mason (1983) suggested that accessibility effects would be important in porous media and attempted to model adsorption-desorption hysteresis by a probabilistic approach. Parlar and Yortsos (1988) and (1989) realized that the process shares common aspects with percolation phenomena and proceeded to explain desorption-adsorption hysteresis, based on the lack of accessibility of liquid-containing pores to bulk (connected) vapor. The following rules were postulated: for phase change to occur in a pore (body or throat), the pore radius first must be consistent with Kelvin's equation (be allowed). At any capillary condensation (adsorption) stage R, given by an equilibrium pressure P_V (equation 2), vapor in all pore bodies with $R_P < R$ and all pore throats with $R_P < R/2$ is *allowed* to condense. Since vapor has access to all of the pores in the network during adsorption, condensation occurs in all pores that are *allowed*. On the other hand, for capillary evaporation (desorption) to take place in a pore with size R_P, the following two conditions must hold: (a) $R_P > R$ and (b) the pore (body or throat) must have access to vapor phase (either to bulk vapor or to a nucleation center). These two rules include the two plausible mechanisms of hysteresis behavior observed in adsorption experiments for porous solids, namely the local (or single-pore) hysteresis [3] and the network (or pore blocking) effect [17]. The first mechanism, reflected above as a difference of 1/2 between adsorption and desorption radii, may appear in pore throats due to the cylindrical geometry. The second mechanism may occur during desorption due to the necessity of having access to vapor. The origin of the second mechanism for hysteresis is due to the topology of the pore space. Depending on the geometry of pore network, evaporation in some large pores may not occur if they are surrounded by small pores that are not allowed to desorb at the particular pressure value.

Recently, the work of Parlar and Yortsos (1988) was expanded by Liu et al. (1993) .

3. Empirical approaches: In relation to the adsorption behavior of steam in The Geysers, many previous studies have been conducted, in-

cluding those by Hsieh (1980), Hsieh and Ramey (1983), Luetkehans (1988), Harr (1991), Hornbrook (1994) and Shang et al. (1994). A recent attempt was made by Correa and Ramey (1994) to explain experimental results with the use of some empirical models. Recent experiments by Satik and Horne (1995) have shown a dramatic temperature effect on hysteresis and the existence of a "residual" value in the amount of desorbed liquid. This cannot be explained convincingly by the work published so far. In this paper, we shall use a pore network model coupled with the theory of Evans et al. (1986) to propose a possible explanation of this effect. More generally, the paper develops a general pore network model for adsorption-desorption processes in porous media.

The paper is organized as follows: First, the pore network model is described. The model results are then compared with the experiments and the sensitivity to effects of temperature and mean pore size is described. Finally, we briefly examine the effect of correlated porespace on the adsorption-desorption behavior.

PORE NETWORK MODEL AND RESULTS

To simulate the process of sorption in porous media, we have made use of a pore network model. We represent the pore space by a 3-D lattice composed of pore bodies (sites) and connections between pore bodies (bonds or pore throats). In this approach, pore bodies and throats are approximated by spherical and cylindrical geometries, respectively. A simple cubic lattice, where six bonds emanate from a site, corresponding to a coordination number of six, is taken (although other lattice types can also be used). Radii for sites and bonds were randomly distributed from a truncated Gaussian random distribution with means 32.5 *nm* and 5.5 *nm*, respectively and standard deviations of 35 *nm* and 9 *nm*, respectively, while the bond length (l_b) was kept constant at 25 *nm*. Adsorption and desorption were modeled following the rules of Parlar and Yortsos (1988).

Adsorption proceeds by multi layer adsorption, modeled via the *FHH* equation, then capillary condensation in sufficiently large pores occurs. We used the modified Kelvin equation for its description. For desorption to occur, the given pore must have size sufficiently large, as predicted by Kelvin's equation or its modifications, but it must also be connected to the bulk vapor. Narrow pores containing supercritical liquid were not allowed to desorb. Owing to stability considerations [17], if a bond is occupied by vapor, the two adjacent sites are also occupied by vapor, while if a site is occupied by liquid, all bonds connected to it are also occupied by liquid.

As discussed above, during a typical sorption experiment for porous solids, a hysteresis behavior is commonly observed. Depending on the process parameters, different types of hysteresis can be expected. Although different in shape, in most cases adsorption and desorption isotherms coincide below a moderate pressure value, indicating the end of hysteretic behavior. However, a rather unusual hysteresis was observed in high temperature steam adsorption experiments conducted in samples obtained from The Geysers geothermal field (see Satik and Horne (1995)). These experiments showed that at higher temperatures, e.g. 120 °C, hysteresis persists down to very low pressures, of order 0.001 psia, while diminishing at lower temperatures. With the use of the pore network model, we have attempted to investigate this behavior and to interpret the effects of temperature. In all simulations presented the size of the network was taken to be 20x20x20, which was found to be sufficiently large to eliminate finite-size effects.

Figure 3 shows two sorption isotherms obtained from the numerical model at 80 and 120 °C. The figure shows a very good agreement with the experimental findings of Satik and Horne (1995). In particular, the two main experimental features are clearly observed in the simulations: A hysteresis persisting down to very small pressures, at high temperature values, and a diminishing of the hysteresis cycle at lower temperatures. Figure 4 shows a comparison of the simulation results with the experiments (for a sample from The Geysers) of Satik and Horne (1995). Figure 4a and 4b shows the experimental results, while Figure 4c and 4d contain the numerical results obtained at 120 and 80 °C, respectively. A very good agreement is shown, considering the experimental errors involved. Figure 5 shows the effect of the mean radius on the adsorption curves. We have examined three cases with mean radius corresponding to 5.5, 6 and 10.5 *nm*,respectively. As shown in the figure, the degree of hysteresis increases as the mean radius decreases. This is expected in view of both the Kelvin equation and the effects of the critical capillary radius. The implication is that the rock samples treated by Satik and Horne (1995) must contain pores of a narrow size (of order of a few

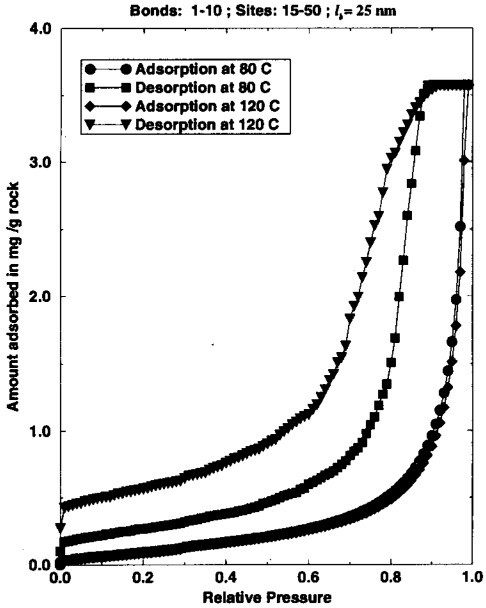
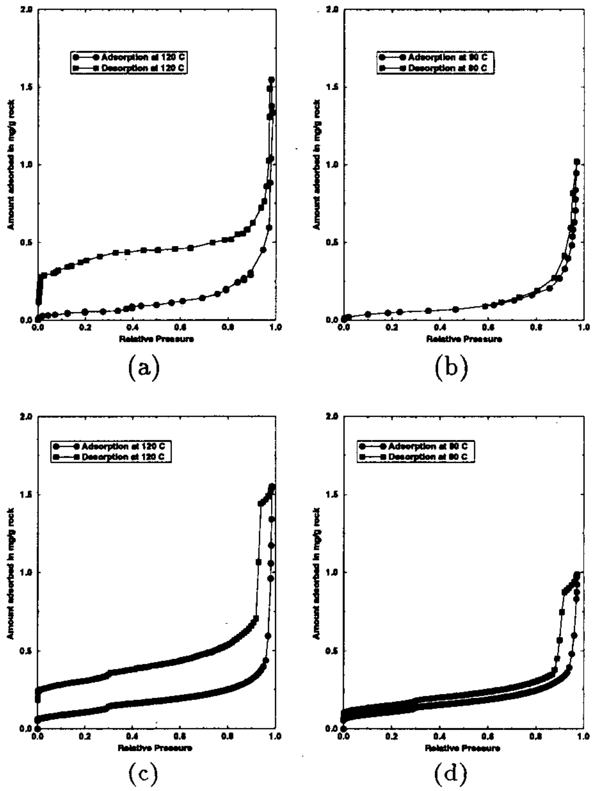


Figure 3: Sorption isotherms in pore networks at 80 and 120 °C.

nm).

Experimental and numerical results show that hysteresis diminishes as the temperature decreases, this is opposite to the trend in a single-pore. We explain this as follows: As temperature increases, the capillary critical radius, below which fluids occupying pore space are supercritical, also increases. This implies that a larger fraction of pores contain supercritical fluid. The fluid density in these pores decreases slowly and monotonically with pressure from an initial liquid-like density to a gas-like density at very small pressures (see curve d in Figure 2). In a pore network, these small pores eventually surround larger pores, preventing them from desorption due to the pore-blocking effect explained above. This behavior results in the hysteresis persisting until very small pressure values, and being a strong function of temperature.

Figure 6 shows a comparison of the sorption isotherms obtained for a fractured and an uncorrelated pore network. A fractured system was generated by assigning two very different average pore size values, with smaller values assigned to the "matrix" and larger values assigned to the "fracture" system. For the results shown in the figure, the fracture sysytem consisted of five orthogonal fracture planes parallel to the three coordinates of the cubic lattice (x=const,y,z), (x,y=const,z) and



(a) (b)

(c) (d)

Figure 4: Comparison of the experimental sorption isotherms (a and b) obtained for a Geysers sample at 120 and 80 °C (from Satik and Horne (1995)) with the results from the pore network model (c and d).

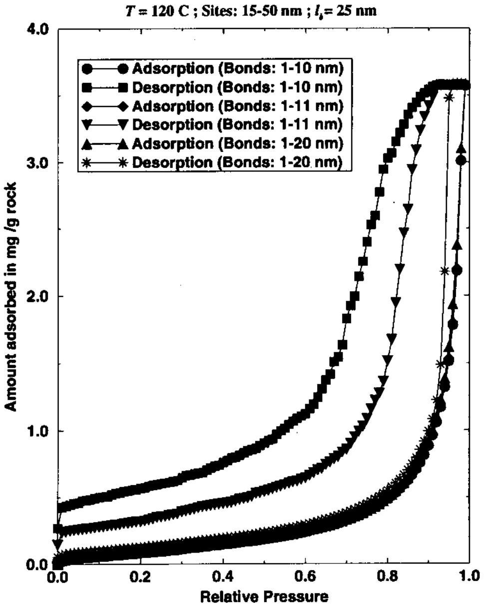


Figure 5: Effect of the mean radius on sorption isotherms in pore networks.

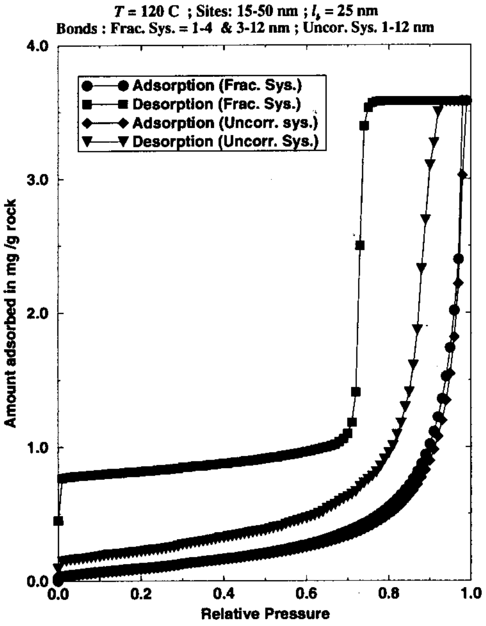


Figure 6: Comparison of sorption isotherms obtained for a fractured and an uncorrelated pore network.

(x,y,z=const), each spanning the whole network and intersecting each other. As shown in the figure, the fractured systems display a pronounced hysteresis behavior compared to uncorrelated systems. This is also due to the pore blocking effect. We must note, however, that the hysteresis behavior shown in Figure 6 will not depend on temperature, hence a fracture network itself would not be able to simulate the experimental results if the previous mechanism involving supercritical fluid is not accounted for.

CONCLUSIONS

We have presented a pore network model that incorporates improved single-pore pheneomena for adsorption and desorption in porous media, particularly the supercritical behavior at narrow pores. The latter accounts for substantial hysteresis which depends sensitively on temperature. The network model gives results in good agreement with the experiments. This hysteresis is attributed to a pore blocking mechanism, where narrow pores containing supercritical fluid prevent larger pores from desorbing, due to lack of access to bulk vapor. Hysteresis is also found to increase in a dual porosity (fracture) system.

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References

[1] Adamson, A. W.: *Physical Chemistry of Surfaces*, John Wiley & Sons, New York (1990).

[2] Aukett, P., Quirke, N., Riddiford, S., and Tennison, S. R.: "Methane adsorption on microporous carbons-A comparison of experiment, theory and simulation," *Carbon* (1992) **30**, 913–924.

[3] Ball, P. C. and Evans, R.: "Temperature dependence of gas adsorption on a mesoporous solid: Capillary criticality and hysteresis," *Langmuir* (1989) **5**, 714–723.

[4] Correa, A. C. and Ramey, H. J., J.: "Theoretical Investigation of adsorption in Porous

media," Submitted to SPE Advanced Technology Series, 1994.

[5] Evans, R., Marconi, U. M. B., and Tarazona, P.: "Capillary condensation and adsorption in cylindrical and slit-like pores," *Chem. Soc. Faraday Trans. 2* (1986) **82**, 1763–1787.

[6] Everett, D. H. and Haynes, J. M.: "Model studies of capillary condensation: I. Cylindrical pore model with zero contact angle," *J. Colloid and Interface Science* (1972) **38(1)**, 125–137.

[7] Gregg, S. J. and Sing, K. S. W.: *Adsorption, Surface Area and Porosity*, Academic Press, London and New York (1982).

[8] Harr, M. S.: "Laboratory Measurements of Sorption in Porous Media," M.S Report, Stanford University, 1991.

[9] Hornbrook, J.: "The effects of adsorption on injection into and production from vapor dominated geothermal reservoirs," Ph.D. Thesis, Stanford University, 1994.

[10] Hsieh, C. H.: "Vapor Pressure Lowering in Porous Media," Ph.D. Thesis, Stanford University, 1980.

[11] Hsieh, C. H. and Ramey, H. J., J.: "Vapor Pressure Lowering in Geothermal Systems," *SPEJ*, Vol 23(1), pp. 157-167, 1983.

[12] Lastoskie, C., Gubbins, K. E., and Quirke, N.: "Pore Size Heterogeneity and the Carbon Slit Pore: A Density Functional Theory Model," *Langmuir* (1993) **9**, 2693–2702.

[13] Leutkehans, J.: "A Laboratory Investigation of Steam Adsorption in Geothermal Rocks," M.S Report, Stanford University, 1988.

[14] Liu, H., Zhang, L., and Seaton, N. A.: "Analysis of sorption hysteresis in mesoporous solids using a pore network model," *Chem. Eng. Sci.* (1993) 285–293.

[15] Mason, G.: "A model of adsorption-desorption hysteresis in which hysteresis is primarily developed by the interconnections in a network of pores," *Proc. R. Soc. London A* (1983) **390**, 47–72.

[16] Nicholson, D.: "Molecular Theory of Adsorption in Pore Spaces," *J. Chem. Soc. Faraday Trans. 1* (1975) **71**, 238–255.

[17] Parlar, M. and Yortsos, Y. C.: "Percolation theory of vapor adsorption-desorption processes in porous materials," *J. of Colloid and Int. Sci.* (1988) **124(1)**, 162–176.

[18] Parlar, M. and Yortsos, Y. C.: "Nucleation and Pore Geometry Effects in Capillary Desorption Processes in Porous Media," *J. of Colloid and Int. Sci.* (1989) **132(2)**, 425–443.

[19] Satik, C. and Horne, R. N.: "An experimental Study of Adsorption in vapor-dominated geothermal systems," To be presented at the Twentieth Stanford Geothermal Workshop 1995, Stanford, CA, Jan. 24-26 1995.

[20] Seaton, N. A., Walton, J. P. R. B., and Quirke, N.: "A new analysis method for the determination of the pore size distribution of porous carbons from nitrogen adsorption measurements," *Carbon* (1989) **27**, 853–861.

[21] Shang, S. B., Horne, R. N., and Ramey, H. J., J.: "Study of water adsorption on geothermal reservoir rocks," Submitted to *Geothermics*, 1994.