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PORE NETWORK MODELING OF ADSORPTION EFFECTS IN GEOTHERMAL RESERVOIRS

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ABSTRACT

Physical adsorption is a major factor governing the behavior of geothermal reservoirs. That is, adsorbed water on the rock surfaces in a geothermal field has been thought to provide a major source of fluid within the reservoir. In addition to this, the effect of carbon-dioxide flow through water is another main concern for geothermal reservoirs. A single pore model was developed to investigate adsorption considering CO_2 presence in water.

Using this model, adsorption effects with CO_2 presence is discussed at varying temperature and pressure. The model is run at temperatures ranging between 90-130°C at different relative pressures. Stanford experimental adsorption data were compared to the results of this developed model. It has been found that, there is a reasonable fit between the experimental data and the model. A critical pore radius that allows vapor molecule to enter the pore was calculated. It has been observed that the amount of CO2 adsorbed as well as water in geothermal fields is considerable.

INTRODUCTION

Geothermal reservoirs which are especially vapor-dominated consist of porous or fractured rock, with the interstitial spaces filled with steam (*Horne et al.*). Because of the occurrences of the adsorption process, water molecules are stored on the surfaces of the pore spaces in a state that is more like that of a liquid than that of a vapor. It is accepted that the performance of a vapor-dominated geothermal reservoir is governed strongly by the effects of adsorption (*Horne et al.*).

The phenomenon of adsorption and desorption at solid/liquid interface is of major importance since it is generally accepted that the wettability of a reservoir can be changed by adsorption. Moreover, working with microporous materials has generally shown that the effects of adsorption are, in fact, important when the pore sizes become small and the ratio of pore surface area to pore volume (PV) becomes large. Due to these facts, the rates of water adsorption and the rates of CO_2 adsorption miscible in water for geothermal fields were analyzed. It is accepted that the performance of a vapor-dominated geothermal reservoir is governed strongly by the effects of adsorption (*Horne et al, 1994*).

The pore network is a representation of the void space of the reservoir rock. Each pore was assumed to be cylindrical or spherical and hence contain just one phase. There are lots of studies concerning pore models in order to observe the permeability, saturation, multiphase flow in a pore network model (*Oren et al, 1997; Fenwick et al, 1997; Blunt, 2001*). Fundamentally, the geometry of the void space of a porous medium and the interactions of the multiple phases with the solid determine macroscopic properties such as porosity, relative permeability, capillary pressure and resistivity index (*Al-Gharbi et a,2003l*).

In this study, the network model idealizes a porous medium as a three-dimensional lattice of a spherical chamber. The network model is reduced to a single pore model which has a volume of approximately 329 μm^3. Then using appropriate methods, adsorption effects on the rock are computed in the network modeling.

It is a fact that, Langmuir equation is the cornerstone of all theories of adsorption. Therefore, in this study, the amounts of adsorbed particles with respect to relative pressures are calculated using Langmuirian isothermal equations. With this approach, monolayer surface adsorption on an ideal surface can be understood. When examining the water adsorption Langmuir type is considered. On the other hand, when CO_2 flowing through water is under consideration, the BET (Brunauer *et al*, 1938 as cited in Do, 1998) isotherms are used to calculate the amount of adsorbents with respect to relative pressures. This is due to the fact that Langmuir type adsorption can not hold for the solution type systems.

BET equations are the extended version of the Langmuir equations for the mixture type systems.
A large number of adsorption isotherm models presented in the literature are generally able to describe the adsorption of water, methane, ethane, propane, activated carbons, and etc. (*Zhou et al, 2004; Busch et a,. 2003; Do et al, 1991; Lucas et al, 2004); h*owever there is a lack of study understanding both adsorption of water and adsorption of CO_2 in water for geothermal conditions.

The first task in this study was, therefore, to compare the existing experimental data on the adsorption of water in vapor-dominated geothermal fields. The next step was to implement calculation methods suitable for the CO_2 presence in water with the same conditions by using a single pore model. Issues to be discussed in this paper are: (1) Principles of the model (2) What is adsorption? (3) Adsorption on homogeneous solid surfaces by using Langmuir Equations (4) BET Isotherms (5) Comparison with the experimental data (6) CO_2-water adsorption

ADSORPTION

Adsorption is a process where molecules from the gas phase or from solution bind in a condensed layer on a solid or liquid surface. The molecules that bind to the surface are called the *adsorbate* while the substance that holds the adsorbate is called the *adsorbent*. The process when the molecules bind is called *adsorption*. Removal of the molecules from the surface is called *desorption* (*Masel, 1996*).

Adsorption is essentially an attraction of adsorbate molecules to an adsorbent surface. Interaction between adsorbate and the adsorbent consists of molecular forces embracing permanent dipole, induced dipole and quadrupole electrostatic effects. For reasons adsorption is nearly always an exothermic process (*Crittenden et al, 1998*).

There are two fundamentally different types of adsorption;

- *Multilayer adsorption* – Consists of several layers of adsorbate on the surface of the adsorbent.
- *Monolayer adsorption* – All the adsorbate is held in close proximity to the solid.

Multilayer adsorption is basically condensation process; attractive interactions between adsorbate molecules cause gases to condense into a liquid like film on top of the molecules in the first monolayer.

In order to quantify how much gas is adsorbed, adsorption isotherms, which are plots of the amount of gas that is adsorbed on a surface as a function of the pressure of the gas at constant temperature, are used. The major adsorption models are: the Langmuir isotherm, Henry's law, the BET (Brunauer-Emmett-Teller) equation, and the Gibbs adsorption isotherm.

LANGMUIR ISOTHERMS

The Langmuir Adsorption Isotherm was derived by Irving Langmuir in 1918 (Do, 1998) in an attempt to describe the chemisorptions of atoms or molecules at a surface.

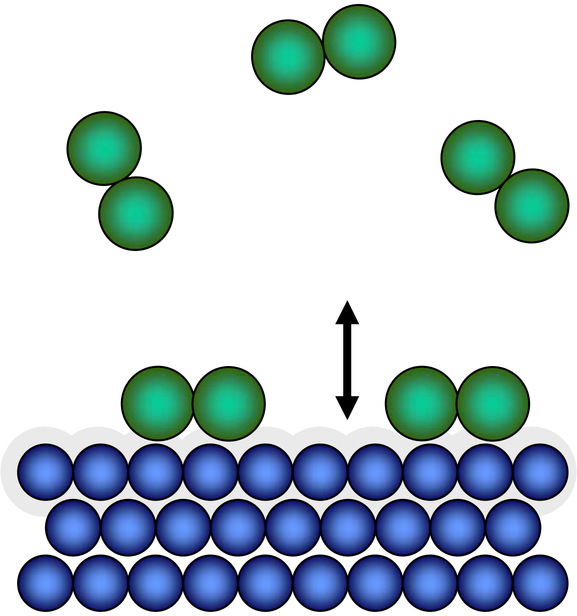

Figure. 1. Schematic diagram of Langmuir adsorption mechanism (Do, 1998).

The assumptions of the Langmuir model (Do, 1998)

1. The surface is homogeneous , that is the adsorption energy is constant over all sites
2. Adsorption on surface is localized, that is adsorbed atoms or molecules are adsorbed at definite, localized sites
3. Each site can accommodate only one molecule or atom

As it is indicated (*Do, 1998*), the Langmuir theory is based on a kinetic principle, that is the rate of adsorption (which is the striking rate at the surface multiplied by a sticking coefficient, sometimes called the accommodation coefficient) is equal to the rate of desorption from surface.

The rate of striking the surface, in mole per unit time and unit area, is:

$$R_s = \frac{P}{\sqrt{2\pi MRT}} \tag{1}$$

Where M is molecular weight, R is gas constant (8.314 J/mol K), π is spreading pressure, T is temperature and P is pressure.

The rate of adsorption, R_a in mole adsorbed per unit bare surface area per unit time when sticking coefficient α is considered is:

$$R_a = \frac{\alpha P}{\sqrt{2\pi MRT}} \tag{2}$$

The rate of adsorption on an occupied surface, that is when a molecule strikes the surface that is already occupied with adsorbed species, is:

$$R_a = \frac{\alpha P}{\sqrt{2\pi MRT}}(1-\theta) \tag{3}$$

Where θ is the fractional coverage.

The rate of desorption, R_d from the surface is:

$$R_d = k_d\,\theta = k_{d\infty}\exp\left(-\frac{E_d}{RT}\right)\theta \tag{4}$$

Where E_d is the activation energy for desorption, that is the heat of adsorption for physically sorbed species and k_d and k_∞ are constants.

Equating the rates of adsorption and desorption will yield the famous Langmuir isotherm in terms of fractional loading:

$$\theta = \frac{bP}{1+bP} \tag{5}$$

Where b is Langmuir constant.

$$b = \frac{\alpha \exp(Q/RT)}{k_{d\infty}\sqrt{2\pi MRT}} = b_\infty \exp(Q/RT) \tag{6}$$

Where Q is heat of adsorption

When the pressure is very low ($bP \ll 1$), the Langmuir isotherm equation reduces to Henry's law isotherm, that is the amount of adsorbed increases linearly with pressure (*Do, 1998*).

If experimental data correlation is taken into account, there will be a need for an equation with amount of adsorbed species instead of fractional loading. In order to have a relation between amounts of adsorbed with pressure, let C_μ be the amount adsorbed phase μ in mole per unit mass and $C_{\mu s}$ be the amount adsorbed concentration of phase μ corresponding to a complete monolayer coverage. Then the Langmuir equation written in terms of the amount adsorbed is (*Do 1998*):

$$C_\mu = C_{\mu s}\frac{b(T)P}{1+b(T)P} \tag{7}$$

where

$$b(T) = b_\infty \exp(Q/RT) \tag{8}$$

BET (BRUNAUER, EMMETT AND TELLER) ISOTHERM

The BET theory was first developed by Brunauer et al. (1938) for a flat surface (no curvature) and there is no limit in the number of layers which can be accommodated on the surface. This theory made use of the same assumptions as those used in the Langmuir theory. Let s_0, s_1, s_2 and s_n be the surface areas covered by no layer, one layer, two layer, and n layers of adsorbate molecules, respectively (*Do 1998*).

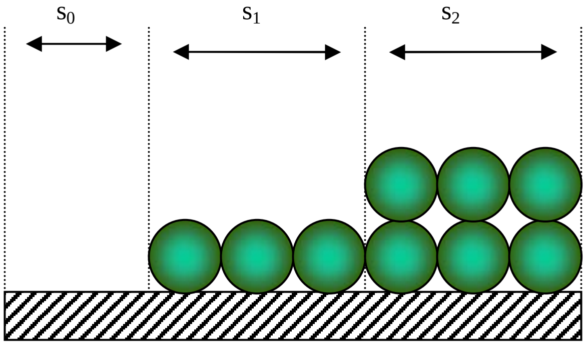

Figure. 2. Schematic Diagram of Multiple layering in BET theory. (Do, 1998)

The concept of kinetics of adsorption and desorption proposed by Langmuir is applied to this multiple layering process, that is the rate of adsorption on any layer is equal to the rate of desorption from that layer (*Do 1998*).So, in general:

$$A_i\,P\,s_{i-1} = b_i\,s_i\exp(-E_i/RT) \tag{9}$$

The total area of the solid is the sum of all individual areas, that is:

$$S = \sum s_i \tag{10}$$

The volume of gas adsorbed on the section of the surface having "i" layers is:

$$V_i = V_m \left(i \frac{s_i}{S}\right) \qquad (11)$$

Hence, the total volume of gas adsorbed at a given pressure is the sum of all these volumes:

$$V = \frac{Vm}{S}\sum_{i=0}^{\infty} is_i = V_m \frac{\sum_{i=0}^{\infty} is_i}{\sum_{i=0}^{\infty} s_i} \qquad (12)$$

An expression for s_i in terms of gas pressure is needed in order to obtain the amount of gas adsorbed as a function of pressure. Therefore, a further assumption should be made. That is the ratio of the rate constants of the second and higher layers is equal to each other:

$$\frac{b_2}{a_2} = \frac{b_3}{a_3} = ... = \frac{b_i}{a_i} = g \qquad (13)$$

According to Langmuir isotherms, it is assumed that the heat of adsorption of the second and subsequent layers are the same and also equal to the heat of liquefaction, E_L:

$$E_2 = E_3 = \ldots.. = E_i = E_L \qquad (14)$$

Therefore, the surface coverage of the section containing I layers of molecules is:

$$s_i = \frac{a_1}{b_1} s_0 \, g \exp(\varepsilon_1 - \varepsilon_L)\left[\left(\frac{P}{g}\right) \exp \varepsilon_L\right]^i \qquad (15)$$

for i = 2,3…, where ε_L is the reduced heat of liquefaction

$$\varepsilon_L = \frac{E_L}{RT} \qquad (16)$$

As a result,

$$\frac{V}{Vm} = \frac{Cs_0 \sum_{i=1}^{\infty} \mathrm{i}\, \mathrm{x}^{\mathrm{i}}}{s_0\left(1 + C\sum_{i=1}^{\infty} \mathrm{x}^{\mathrm{i}}\right)} \qquad (17)$$

where the parameter C and the variable x are defined as follows:

$$y = \frac{a_1}{b_1} P \exp(\varepsilon_1) \qquad (18)$$

$$x = \frac{P}{g} \exp(\varepsilon_L) \qquad (19)$$

$$C = \frac{y}{x} = \frac{a_1 g}{b_1} e^{(\varepsilon 1 - \varepsilon L)} \qquad (20)$$

The equation then can be simplified in the following form:

$$\frac{V}{Vm} = \frac{Cx}{(1-x)(1-x+Cx)} \qquad (21)$$

In order to relate this equation with pressure instead of x, the procedure is as follows:

This model is valid for infinite layers on top of a flat surface. Therefore, the amount adsorbed must be infinity when the gas phase pressure is equal to the vapor pressure, that is $P = P_o$ occurs when $x = 1$. Thus,

$$x = \frac{P}{P_0} \qquad (22)$$

$$\text{where } P_0 = g \, . \exp\left(-\frac{EL}{RT}\right) \qquad (23)$$

So, the infamous BET equation containing two fitting parameters C and V_m becomes:

$$\frac{V}{Vm} = \frac{CP}{(P_0 - P)(1 + (C-1)(P/P_0))} \qquad (24)$$

Where P_0 is the vapor pressure.

PRINCIPLES OF THE MODEL

The single pore model is a perfect sphere which has a volume of approximately 329 μm^3. The pore radius (4.28 μm) is a typical average value observed in sandstones. Initially, the pore is saturated with water. Initially water adsorption occurs. The amount of water adsorbed is calculated using the aforementioned Langmuir model. The vapor pressures for the working temperatures (90°C-130°C) are gathered from literature. The next step is to compute the amount of adsorption due to the CO_2 in presence of water. Thus, CO_2 is introduced into the pore at a fixed rate. It is assumed that CO_2 is completely dissolved in water at the moment it is introduced into the pore. At this stage entire pore is filled with the CO_2 – water mixture. Therefore, the amount of liquid and gas phase in the pore is known both for the water and the CO_2 – water mixture. It is assumed that BET equations are valid. The vapor pressure of the CO_2 – water solution is computed using Raoult's equations. In both adsorption stages there are no chemical reactions that will lead to solution and deposition of silica. The final assumption is that the temperature of the pore does not change during the process.

COMPARISON OF THE CALCULATED AMOUNT OF ADSORBED WATER WITH THE EXPERIMENTAL DATA

In this part, the amount of adsorbed water from the literature was compared with the proposed model. The comparison was made with high pressures and temperatures.

Fig. 3 shows the trend of amount of adsorption of water with varying temperatures in a core from the Geysers MLM-3 (Horne et al, 1994). It can be seen that there is a linear behavior below relative pressures of 0.6.

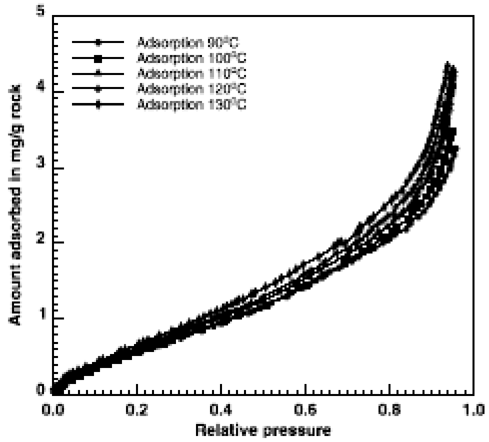

Figure 3: Adsorption Isotherms on Geysers MLM-3 Sample at Different Temperatures (*after Horne et al*, 1994)

Fig. 4 shows the amount of water adsorbed as a function of relative pressure calculated using the proposed single pore model. The total amount of water adsorbed increases as the temperature increases. This is expected as adsorption is an exothermic process. For relative pressure values below 0.6 the model results also show a linear trend. When the amounts of adsorbed values were compared, a reasonable fit was obtained. There is an error of less than %7 when the experimental data is compared with the proposed method. For relative pressures above 0.6, model adsorption values start to deviate and the error between the computed data and the experimental data becomes significantly high (more than %25). Moreover, it is observed that when temperature and pressure increase the error becomes higher. This may occur due to the fact that Langmuir type isotherms assume monolayer coverage. However recent results show that at high pressures there may be more than just monolayer coverage (*Knight et al.,2005*).

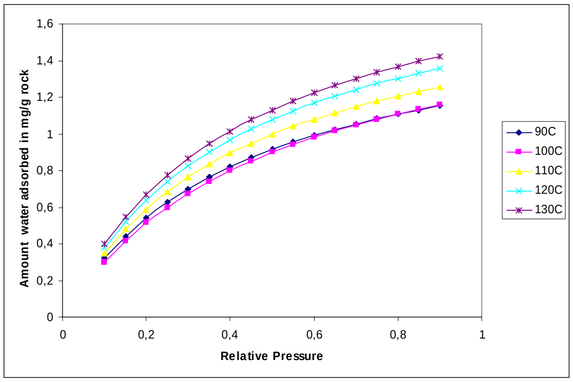

Figure 4: Calculated Adsorption Isotherms for Geysers MLM-3.

CO_2-WATER ADSORPTION

The next step is to investigate adsorption of CO_2 with presence of water since aqueous solutions that contain volatile (gas) components are one of the most important types of fluid in the Earth's crust (*Diamond, 2001*). After primary adsorption of water the secondary adsorption of CO_2 in the same pore was investigated. CO_2 mole percent was fixed at 5 and the relative vapor pressure of the mixture was calculated according to this assumption. BET isothermal equations were used to calculate the amount of adsorbed values for both CO_2 and water.

The solubility of CO_2 decreases with rising temperature, but increases sharply with rising pressure up to the saturation pressure and a lesser rate thereafter (*Spycher 2003*). Qualitatively, the adsorption process of CO_2 follows the same trend. Fig. 5 shows the relationship between pressures ranging between approximately 5kPa to 44.5kPa. In this figure, a linear function up to a relative pressure of 0.2 was observed. But, after that point, there is a rapid increase in the amount of CO_2 adsorption. Since adsorption is an exothermic process, the amount of adsorbed CO_2 increases as the temperature increases.

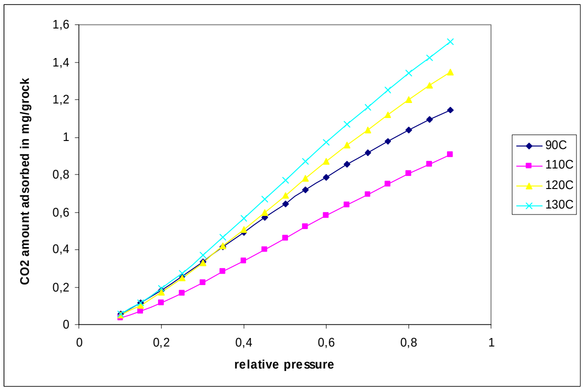

Figure 5: Calculated CO_2 Adsorption isotherms

Fig. 6 shows the comparison of the adsorption tendencies of water and CO_2-water solution at 90°C. It is easily observed that amount of adsorbed water is higher than that of CO_2 at the same temperature and pressure. The major dissimilarity between CO_2 and water adsorption arises from the fact that CO_2 molecules are large and non-polar, whereas H_2O molecules are small and dipolar.

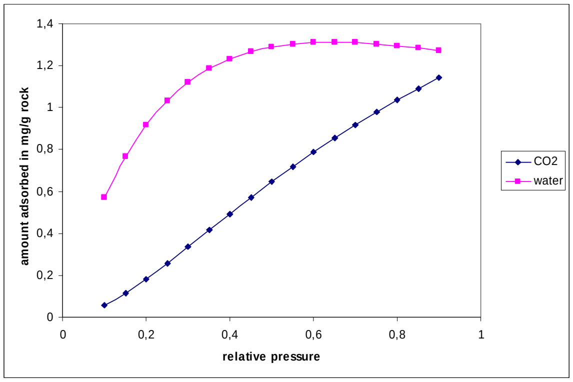

Figure 6: Comparison of adsorbed amounts at 90°C

Although there are dissimilarities between CO_2 and water in their physical properties, both water and the CO_2-water solution isotherms had increasing trends during adsorption processes. Fig. 7 shows the adsorption isotherm calculated at 130°C. When the trends both at 90°C and 130 °C were compared, it is observed that both isotherms have the same trend; however, at the same pressures, the liquid amount adsorbed by the rock for the high temperature is more then the low temperature. Moreover, at the same pressures, the liquid amount adsorbed by the rock for secondary adsorption process was less than that of water in the primary adsorption. The adsorption behavior is determined by the ratio of the fluid-wall attractive interaction. For water this ratio is very small, due to the strong hydrogen bonding (H-bonding) between water molecules. (*Brennan et al. 2001*). The rapid increase of adsorbed molecules in mixture at higher pressures is due to the accuracy of BET equations at higher pressures. This rapid increase is a result of capillary condensation.

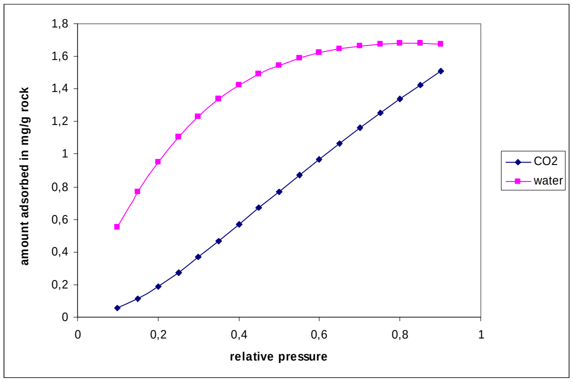

Figure 7: Comparison of adsorbed amounts at 130°C

Critical radius r_c, which is equivalent to the radius of space extended by a steam molecule, r_g, at a given temperature and pressure is a concern to be discussed in an adsorption process. Because of the fact that, this value of radius controls the entrance of the vapor molecule a pore with a radius smaller than r_c can not be filled with the vapor since capillary condensation cannot take place. In order to find out this critical radius, this procedure is used for several pore radii and it is obtained that, within this method the critical pore radius should be as 2.98 μm.

CONCLUSION

In this paper, a simple single pore model, taking advantage of Langmuir and BET isotherms has been presented to calculate the adsorption of water alone and in the presence of carbon dioxide. A comparison of the adsorption of water with the literature data and an approach which deals mainly with the tendency of adsorbed amounts of CO_2-water mixtures towards higher pressures and temperatures is presented. It was observed that for low relative pressures (<0.6) the model agrees well (less than %7) with the published data. For high relative pressures the difference was more than %25. It is concluded that water adsorption is more pronounced in a pore filled with water only when compared to a pore filled with both water and CO_2.

This article has stressed adsorption phenomenon to understand the fluid inclusion behavior and to interpret adsorption properties of water and carbon-dioxide. One of the keys to extracting this information lies in understanding the phase relations of the relevant fluid systems.

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