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Mathematical Modeling of Coal Bed Methane Generation

B.Nalinikant[1], B. Gopal Krishna[2], M. Jagannadha Rao[3]

[1]Department of Geology, Andhra University, Visakhapatnam 530003, India

[2]HLDEPP Laboratory, School of Studies in Physics and Astrophysics, Pt. Ravishankar Shukla University, Raipur 492008, India

[3]Department of Geology, Andhra University, Visakhapatnam 530003, India

Abstract: ***Coal-Bed Methane reservoirs have a number of unique features compared to porous or fractured gas reservoirs. Here, the paper presents 2-D mathematical model of coal bed methane generation/storage based on the theories of surface physical chemistry such as Langmuir adsorption isotherm. In this paper, Gibbs isotherm, Langmuir adsorption isotherm, porosity and surface excess are used to derive a formula which is helpful in simulating the generation of Methane adsorbed by coal beds in a real time scenario by assuming gas as ideal gas. Here, results are verified by plotting graphs and then comparing them to field data.***

Keywords: Langmuir adsorption isotherm, CBM (Coal Bed Methane), Gibbs isotherm, time relation τ .

1. Introduction

Coal-bed methane is both potential valuable energy resource and a hazard in active coal mines [1]. Coal-bed methane transport is controlled by a complex set of interacting processes. Unlike the conventional natural gas reservoirs, coal seams are both source rocks and reservoir rocks. Almost all geological strata contain gases. These gases may be released by underground mining activities after in concentrations too small to be of concern. Coal bed methane (the gas emitted from coal which is primarily methane with minor amounts of heavier hydrocarbons, carbon dioxide, nitrogen, oxygen, hydrogen and helium) is a chief component of fire damp in a coal mine. Coal bed methane (CBM) is viewed as a fuel with many environmental advantages because of the lower level of sulphur oxides, hydrocarbons and carbon mono-oxide, it releases when combusted. Methane primarily resides in the phyteral pores and micro pores as well as inthe coal matrix and hence the diffusion rate is very low at the temperature found in mines. The adsorption potential of coal is awesome, allowing it to contain very large amount of gas. Methane bearing coals are considered to be a significant gas resource. Although coal is a porous medium, permeability is usually quiet low and the pore structure is considerably more complex than the usually found elastic reservoirs. Therefore, the increasing importance of coal seams as gas reservoirs, attention is being focused on fracture patterns in coal matrix [2].

1.1. Coal-Bed Methane

Coal is unique in its behavior as it acts as a source/reservoir rock. Coal-Bed Methane (CBM) or coal bed gas is a form of natural gas extracted from coal beds. The term refers to methane adsorbed into the solid matrix of the coal. It is called as ‘sweet gas’ because of its lack of hydrogen sulfide. The presence of this gas is well known from its occurrence in underground coal mining, where it presents a serious safety risk. Coal Bed Methane, often referred to as CBM, it distinct from typical sandstone or other conventional gas reservoir, as the methane is stored within the coal by a process called as adsorption. The methane is in a liquid state, lining the inside of pores within coal (called the matrix). The open fractures in the coal called the cleats can also contain free gas or can be saturated with water. The methane primarily resides in the phyteral pores and micro pores, as well as in the adsorbed state on the carbon complex in the coal matrix. With minor amounts of heavier hydrocarbons, carbon dioxide, nitrogen, oxygen, hydrogen and helium is the chief component of fire damp in a coal seam. Coal Bed Methane evolves during the transformation of the organic matter in the swamp, which later converts into peat after burial under reducing condition. As temperature increases, the peat converts into lignite followed by sub- bituminous, bituminous low-volatile, medium volatile, high-volatile bituminous, anthracite and graphite. This process is known as “coalification”. During this process at early stage biogenic methane evolve, later thermogenic methane is evolved, later thermogenic methane is evolved/formed. Much of the methane generated by the coalification process escapes to the surface or migrates into adjacent reservoirs or other rocks, but a portion is trapped within the coal itself. In early stages of coalification, biogenic methane is generated as a by-product of bacterial respiration. Aerobic respiration (those use oxygen in respiration) first metabolize any free oxygen left in the plant remains and surrounding sediments. In fresh water environments, methane production begins immediately after the oxygen is depleted. Species of anaerobic bacteria (those do not use oxygen), then reduce CO_2 and produce methane through anaerobic respiration.

When a coal’s temperature underground reaches about 122°F and after a sufficient amount of time, most of the biogenic methane has been generated and two-third of the original moisture has been expelled, the coal attains an approximate rank of sub-bituminous. As the temperature increases above

122°F through increased burial or increased geothermal gradient, thermogenic processes begin and additional water, CO_2, and nitrogen are generated as coalification proceeds to approximately the rank of high- volatile (rank), bituminous. Maximum generation of CO_2 with little methane generation occurs at about 210°F. Generation of thermogenic methane begins in the higher ranks of the high volatile bituminous coals and at about 250°F, generation of methane exceeds the generation of CO_2. Maximum generation of methane from coal occurs at about 300°F. With even higher temperatures and higher rank coals, methane is still generated, but at somewhat lower volume [3].

2. Coal Micro Structure and Micro-Permeability and its Effects

2.1. Coal Micro Structure

The micro structure plays a vital role for the flow of methane gas from coal seams. These micro structures fall within the limits of meso- and macro porosity. By the help of scanning electron microscope examination, micro structure shows three porosity types. They are fracture porosity, phyteral porosity and matrix porosity.

Fracture porosity is generally associated with bright coals although micro fractures are present in maceral fragments from the dull coal types/layers. Characteristically the macro and micro fractures form a continuous structural fabric through the bright coal layers. In contrast, phyteral and matrix porosity are associated with the dull coal layers that are composed of plants fragments or heterogeneous mixture of macerals. The continuity of the observed micro meter sized fractures and cavities suggest that they make a significant contribution to overall permeability and therefore play a major role in the transmissibility of methane at a level between diffusion at the micro pore level and laminar flow at the cleat level. The effectiveness of gas drainage through the observed micro structures however is likely to vary according to:-

1. The type of micro structure present in coal type.
2. The degree of coalification.
3. The amount of infilling in the voids.
4. Micro structures density, orientation and continuity.
5. The presence or absence of clay layers in the coal seam [4].

2.2. Coal Methane sorption related to coal composition

Gas sorption by coal is closely related to its composition (physical and chemical properties), which are, in turn governed by coal type and rank. The role of coal type (maceral composition) is not fully established but it is clear that coal type may affect both adsorption desorption rate.

Adsorption capacity is closely related to micro pore (pore < 2nm) development, which is rank and maceral dependent. Adsorption isotherm indicates that in most cases bright (vitriniterich) coals have a greater adsorption capacity than their dull (often intertinite-rich) equivalents.

Desorption rate investigations have been performed using selected bright and dull coal samples in a high pressure microbalance. Interpretation of results using unipore and bidisperse pore models indicates the importance of the pore structure. Bright, vitrinite-rich coals usually have the slowest desorption rates which is associated with their highly micro porous structure. However, rapid desorption in bright coals may be related to development of extensive, unmineralised fracture systems. Both macro and micro pore systems are implicated in the more rapidly desorbing dull coals. Some dull, inertinite-rich coals may rapidly desorb due to a predominance of large, open cell lamina. Mineral matter is essentially non adsorbent to coal gas and acts as simple diluents. However, mineral-rich coals may be associated with more rapid desorption [5].

2.3. Role of coal type and rank on methane sorption characteristics

Coal seams differ from conventional gas reservoirs in several important aspects-

1. Coal seam permeability is almost entirely due to cleat (regularly spaced parallel fractures). Therefore two cleat systems (face cleat and butt cleat) which are nearly orthogonal to one another and are both normal to the bedding plane. Cleat spacing is in millimeter to centimeter range.

2. Coal seams are highly anisotropic; face cleat permeability is usually five to ten times greater than butt cleat permeability.

3. Macro and micro pores (including cleat) are usually responsible only for a small part of the total pore volume, while the greater part (80% and more) is due to micro pore 20Å in diameter and below. Most methane present in a coal seam is initially located in these micro pores i.e. in the matrix rather than in fracture in an adsorbed state. Therefore coal seams usually contain much more methane than a gas reservoir with comparable pressure and porosity.

4. Since micro pores are so narrow, methane movement in micro pores cannot be described as Knudsen diffusion or probably, even slower diffusion mechanisms.

5. Due to the fracture nature of the permeability, it should be more sensitive to pressure changes than conventional reservoir permeability. On the other hand, coal-matrix shrinkage with methane desorption has been reported, which is accompanied by the increase of permeability according to rank. In high volatile bituminous coals, increase in vitrinite content is associated with increases in adsorption capacity. At ranks, higher than medium to low volatile bituminous, changes in maceral composition may exert relatively little influence on adsorption capacity. The Langmuir pressure (P_L) with increasing rank, which was not related to coal type. It is suggested that the observed trend is related to a decrease in the

heterogeneity of the pore surfaces and subsequent increased coverage by the adsorbate, as coal rank increases. Desorption rate studies on crushed samples show that dull coals desorbs more rapidly than bright coals and that desorption rate is also a function of rank. Coals of low rank have effective diffusivities [6].

3. Present Scenario

Investigation on Coal Bed Methane gas shows that in present scenario, the study has been done towards the flow of gas (Methane) in the coal beds based on equations of state and Langmuir isotherm [7-10]. In this paper, we are focusing more on the study of generation of methane gas rather than on the flow of gas in the coal beds and it have been given by deriving a formula on the basis of physical chemistry.

4. Objectives

1) The 2-D mathematical model for Coal Bed Methane generation is presented here on the basis of Langmuir isotherm.
2) Gibbs isotherm gives the relationship between pressure, surface tension and surface excess which gives the pressure exerted by the liquid on the CBM.
3) The porosity of a porous medium (such as rock or sediment) describes the fraction of void space in the material, where the void may contain, such as, air or water. So, it is also added to the volume of the gas because the gas resides inside this void.
4) The total volume of the gas is derived from the above statements and results are verified by isotherm graphs.

5. Methodology

1) The equation for the generation of methane gas in coal beds can be derived from Langmuir adsorption equation because adsorption process dominates throughout the gas generation during coalification.
2) The coal framework is mainly deformed by effective stress resulting from the reservoir pressure reduction. The stress induced changes in both porosity and permeability have been expressed to have the volume of gas in fracture system [7].
3) Coal seams are highly anisotropic, so two components are assumed within the coal seams mainly methane and water.
4) For the grade of the coal, Gibb's equation is applied because grade itself shows feasibility or spontaneity of chemical reaction, where rank and maceral composition (vitrinite) are taken as an ideal constituents.
5) As the time increases, gas content increases and higher rank coal occurs. So sorption time τ and activation energy are considered to get the average methane concentration.

5.1. Mathematical equation of Coal-Bed Methane Generation/storage

Langmuir isotherm

The simplest physical possible isotherm is based on the three assumptions:

1) Adsorption cannot proceed beyond monolayer coverage.

2) All sites are equivalent and the surface is uniform (that is, the surface is perfectly flat on a microscopic scale).
3) The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites [11].
4) From this, the dynamic equilibrium is

$$A(g)+M(surface)\rightarrow AM(surface)$$

With rate constants K_a for adsorption and K_d for desorption.

Suppose, θ be the fraction of the total surface covered by adsorbed molecules at any instant, then the fraction of surface bore available for adsorption is $(1-\theta)$. Since according to kinetic theory of gases, the rate at which molecules strike unit area of a surface is proportional to the pressure of the gas, the rate of condensation of molecules should be determined both by the pressure and the fraction of surface bore, or

Rate of condensation = $K_1(1-\theta)P$

Where K_1 is a constant of proportionality. On the other hand, if K_2 be the rate of evaporation, i.e. the rate at which molecules evaporate from unit surface when the surface is fully covered then for a fraction of surface covered,

Rate of evaporation = $K_2\theta$

The rate of change of surface coverage due to adsorption is proportional to partial pressure P of A and the no. of vacant sites $N(1-\theta)$, where N is total number of sites :

$$\frac{d\theta}{dt}=K_a N(1-\theta) \tag{1}$$

Similarly,

$$\frac{d\theta}{dt}=K_d N\theta \tag{2}$$

At equilibrium Eqn 1= Eqn2

i.e., at equilibrium there is no net change (the forward reaction is equal to the backward
reaction)

$$\theta=\frac{K_p}{(1+K_p)} \tag{3}$$

Where,

$$K_p = \frac{K_a}{K_d}$$

$$\theta = \frac{V}{V_L} \quad (4)$$

V_L = volume of adsorptate corresponding to complete monolayer.
V = total volume at equilibrium

Most of the gas in coal is stored by adsorption in the coal matrix. As a result, pressure-volume relationship is defined by the desorption or adsorption isotherm and not by real gas law [12]. A sorption isotherm relates the gas storage capacity of a coal to pressure and depends on the rank, temperature, and the moisture content of the coal. The isotherm can be used to predict the volume of gas that will be released from the coal as the reservoir pressure is reduced. A common assumption is that the relationship between gas storage capacity and the pressure can be described by an equation represented by Langmuir.

By further calculations we have

$$V = \frac{V_L P}{P_L + P}$$

V_L and P_L are Langmuir volume and pressure.

$$K_P = \frac{\theta}{1-\theta} \quad (5)$$

For grade of the coal, value of K plays an important role. Different values of K are obtained at different temperatures. So temperature dependence of K can be used to determine isosteric enthalpy of adsorption ΔadH. So the use of vant hoff equation to write-

$$\frac{d\ln K}{dt} = \frac{\Delta adH}{RT^2}$$

From Eq 5

$$K_P = \frac{\theta}{1-\theta}$$

$$\ln K + \ln P = cons\tan t$$

$$\frac{d\ln K}{dt} = -\frac{d\ln P}{dt} \quad (6)$$

$$\frac{d\ln P}{dt} = \frac{\Delta adH}{RT^2}$$

The coal frame work will be deformed by the increase in effective stress resulting from the reservoir pressure reduction. The stress induced changes in both porosity and permeability have been expressed by Schwerer and Pavone as [7]

$$\frac{\Phi_f}{\Phi_{f_o}} = e^{c_f(P-P_0)} \quad (7)$$

Φ_{f_o} = initial fracture porosity, Φ_f = final fracture porosity, c_f = pore volume compressibility, P_o = vapor pressure.

By superimposing the effects of pore compressibility and matrix shrinkage, the final expression for porosity and permeability are [7]

Fracture porosity induced by coal matrix

$$\frac{k_f}{k_{f_o}} = \left(\frac{\Phi_f}{\Phi_{f_o}}\right)^3 \quad (8)$$

Where k_f = fracture permeabity, k_{f_o} = fracture permeability at initial time Gibbs energy gives the spontaneity or feasibility of the chemical reaction. If the value of $G(P_f) - G(P_i)$ is negative than reaction is not complete and if it is positive, reaction is positive. So we have following equation [11]

$$G(P_f) = G(P_i) + RT\int_{P_i}^{P_f} \frac{dP}{P} \quad (9)$$

Where $G(P_f)$ and $G(P_i)$ are Gibbs energy at P_f final pressure and P_i initial pressure.

The relation between the change in surface tension and the composition of a surface (expressed by surface excess) was derived by Gibbs. In the following justification we derive the Gibbs isotherm, between the changes in the chemical potential of the substances present in the interface and the change in surface tension [11].

$$dy = \Gamma d\mu \quad (10)$$

Where dy = surface tension, Γ = surface excess, $d\mu$ = chemical potential.

If the concentration of a species j is uniform right up to the interface, then from its volume we would conclude that it contains an amount $n_j(a)$ of j in phase and an amount $n_j(b)$ of j in phase. Where a and b are two phases in contact. However, a species may accumulate at the interface, the total amount of j differs from the sum of these two amounts by $n_j(\sigma) = n_j(a) - n_j(b)$. This difference is expressed by surface excess, Γ [11]

$$\Gamma = \frac{n(j)}{A} \quad (11)$$

A = surface area, $n(j)$ = one component in an overall amount for a system of several components j.

By Gibbs isotherm, we have [11]

$$dy = \Gamma RT \int_{P_i}^{P_f} \frac{dP}{P} \tag{12}$$

Where

$$d\mu = RT \int_{P_i}^{P_f} \frac{dP}{P} \tag{13}$$

For a particular component of liquid in a capillary we have

$$A = \frac{RT}{y} \int \frac{\ln P}{P_o} dn$$

$$\frac{Ah}{x} = \frac{RTh}{xy} \int \frac{\ln P}{P_o} dn \tag{14}$$

Where h =depth of the coal seam, x = thickness of coal sheet
From equation 5,7 & 14

Pressure and volume relation plays an important role for determining the filling of the voids [13]. The surface exposed to gas and other things is constant bombarded with molecules and a freshly prepared surface is covered very quickly [11]. This is due to the no. of collisions which is determined by collision flux Z_w.

Total gas in coal = absorbed gas + gas in the fracture system (-/+)volume of liquid/gas in the system

$$V_e = \left(\frac{V_L P}{P_L + P} \right) + V_L \Phi_{f_o} e^{c_f (P - P_o)} - V_L \Phi_{\lg} Z_w \left(\frac{RTh}{xy} \right) \int \frac{\ln P_{\lg}}{P_o} dn \tag{15}$$

$$V_e = \left(\frac{V_L P}{P_L + P} \right) + V_L \Phi_{f_o} e^{c_f (P - P_o)} - V_L \Phi_{\lg} Z_w \left(\frac{RTh}{xy} \right) \left(\frac{\ln P_{\lg}}{P_o} \right) \left(\frac{n_f - n_i}{N_A} \right) \tag{16}$$

Where $\Phi_{\lg}$, Z_w & $P_{\lg}$ are the content of the liquid/gas, collision flux & pressure of the liquid/gas exerted on the surface of solid respectively.

If an activated species C of volume V_c gas as it binds with a transported species A of volume V_A gas then dissociation of AC is such that,

$$AC \rightarrow A + C$$

$$k = \frac{[A][C]}{[AC]}$$

For the equation $C_o \rightarrow C + AC$, where V_{C_O} is the final concentration of the transported species, then, by calculations

$$[AC] = \frac{[A][C_o]}{A} + k$$

Hence the rate of diffusion of gas J can be given by fick's law as [14]

$$J = \frac{dV_{C_o}}{dt} = k_{AC} \tau_{AC} \left\{ \frac{V_A}{V_A + K} \right\} \left(\frac{1}{h} \right)$$

differentiating the above equation w.r.t. t

$$\ln V_{C_o} = k_{AC} \tau_{AC} \left\{ \frac{V_A}{V_A + k} \right\} \left(\frac{t}{h} \right) + c \tag{17}$$

where $k_{AC} = \frac{[AC]_o}{[AC]_s}$ and $c = \frac{([A]_o + K)}{[A]} * [AC]$

Where, V_{C_o} is transported matrix gas concentration, τ is sorption time (days); V_e is the equilibrium methane concentration described by Langmuir isotherm, $\tau_{AC} = 5 days$, $[A]_o$ or V_{Ao} and $[C]$ or V_C = initial concentrations of A and C , $[A]$ or V_A and $[C]_o$ or V_{C_o} = concentrations of A and C at time t, $[AC]_s$ or and [AC]s or V_{AC_S} = concentrations in the bulk of the whole system.

6. Nomenclature

A =surface area
c_f = pore compressibility
$d\mu$ = chemical potential
K_a = Adsorption constant
K_d =Desorption constant
k_f = fracture permeability
k_{f_o} = initial fracture permeability
K = Rate Constant
$n(j)$ = one component in overall amount for a system of several components j.
N_A =Avagrodro number
P= Pressure (Pa)
P_o =vapour pressure of fluid
P_L = Langmuir pressure
θ = Rate of change of surface coverage due to adsorption
ΔadH = enthalpy of chemisorptions and physisorption.
R = Gas constant (8.31Jmol^{-1}K^{-1})
T = absolute temperature
V_e = Total volume at equilibrium
V_L = Langmuir volume
Φ_f = fracture porosity

Φ_{fo} = initial fracture porosity
Γ = surface excess
x = thickness of the sheet of coal seam
τ =desorption time

7. Results and Discussion

Based on the acquisition of relevant reservoir parameters by means of adsorption laws, complete data for gas production and water drainage were obtained after reservoir stimulation. The presented mathematical model was solved simultaneously by the fully implicit method and a relevant reservoir simulator was also developed to simulate the CBM Well on south Qinshui basin. The simulation parameters are listed in Table 1.

The graph have been drawn by taking some assumed values based on the data given on adsorption and some other references [8]. Some of the standard values are estimated from references [7,13,15]. History data matching was done to stimulate the gas production w.r.t. time and a graph is plotted between these parameters by using the equations 16 and 17. From the graph (figure1), the calculated values of gas production on increasing time are nearly consistent with the field data. Initially the gas production increases rapidly but after some days the production of gas decreases and become constant with increase in time assuming the values of pressure and temperature to be taken as constant.

Table1-Parameters of coalbed methane reservoir simulation

With values of reservoir pressure 3.17 MPa, Langmuir pressure 0.31 MPa, Langmuir volume 35.0 m^3/t, Porosity 0.21 f, coal thickness 7.23m, burial height 472.37m, reservoir temperature 23^oC, primary water saturation 0.79, water pressure 40 MPa, and gas water pressure 24MPa.

Time (days)	Daily production m^3/day
1	181.8
40	359.5
80	698.5
120	979.3
160	1149.3
200	1889.4
240	1333.5
280	1209.6
320	3078.1
360	2234.5
400	1521.3
440	1390.5

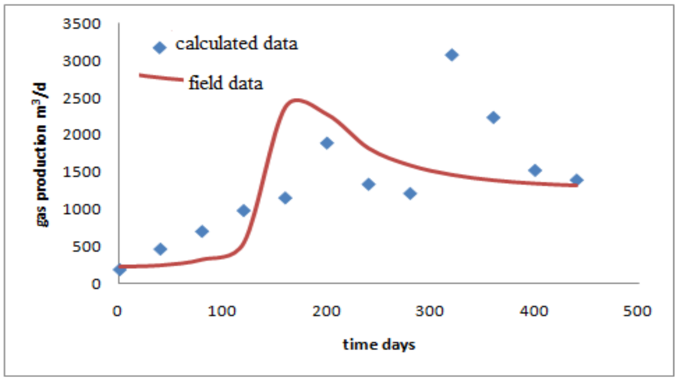

Figure 1: History curve for the gas production rate for the south Qinshui basin

8. Conclusion

This attempt has been made to derive a formula with the help of adsorption isotherm principle such as Langmuir isotherm to know the generation of methane gas in coal seams. The 2-D model representation of the formula helps us to know the role of all the parameters as discussed above. This can be explained in the real time scenario as well, with some assumptions. The formulae is also useful to proceed with the 3-D model of the situation and attempts are being made to make this type of model by the principles of statistical and quantum mechanics which will further replicate the exact situation in the coals seams. Although values in this paper are taken from references, the formulae developed in this investigation can be applied in the real time scenario to understand CBM generation from adsorbed particles. However the gas needs to be considered as an ideal gas [12]. It is established that this kind of approach will have a potential applicability in understanding the complex CBM reservoirs, by mathematically simulating them by such modeling studies.

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