CARBON BED INTERFLOW PERFORMANCE PREDICTION USING VARIABLE HYPOTHETIC PRESSURE WAVE CYCLES MODEL

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First Registered on 7 August 2009; Received after Corection on 21 October 2009
Publication Approval on : 25 November 2009

ABSTRACT

The nature of low productivity of CBM well experiences represent low interflow performace over matrix and fractures in coal bed. Therefore, to increase CBM well production rate, it is necessary to improve the interflow performace.

An approach to improve the interflow performance is to find out the possibility of increasing gas flowrate in carbon bed taken into account factors dominantly effect on the performance. For this purposes, Variable Pressure Wave Cycles Hypothetical Model has been developed based on Pressure-Swing adsorption - desorption (PSA) technique commonly applies in natural gas separation using carbon active bed. Preliminary simulation of the model has been carried out using data related to carbon bed taken from previous studies. Variables in the simulation are kinetic constant and hypothetic pressure waves generated which is required to increase gas flow rate in the bed.

The simulation results demonstrate the possibility of interflow performance improvement in carbon bed. However, this improvement is asymptotically limited to maximum amount of gas desorbed from carbon bed as well as Langmuir Isotherm pattern application for gas desorption from coal.

Moreover, the simulation of the model shows the sensitivity of gas interflow performance to hypothetical pressure waves generated and kinetics controlling adsorption/desorption mechanism and mass transport in carbon bed.

Key words: carbon bed interflow-pressure wave cycles

I. BACKGROUND

Coal Bed Methane (CBM) has been considered as one of domestic energy resources in Indonesia. CBM pilot project has been running since 2003 with CBM production target has been set to achieve around 100 MMSCFD in 2014. Meanwhile, having been dewatering for 24 to 36 months, US experiences in CBM production rate averaging about 120 Mcfd/well to 800 Mcfd/well[8]. This experience will indicate potential problems that may be encountered to achieve 100 MMSCFD CBM production rate in Indonesia due to the low productivity of CBM well.

Since methane is stored in CBM reservoir, the nature of low productivity of CBM well represents low interflow performace over matrix and fractures in coal bed. Therefore, to increase CBM well production rate, it is necessary to improve interflow performace in the bed.

An approach to improve the interflow performance is to find out the possibility of increasing gas flowrate in carbon bed taken into account factors dominantly effect on the performance. For this purposes, Variable Pressure Wave Cycles Hypothetical Model has been developed based on Pressure-Swing adsorption - desorption (PSA) technique commonly applies in natural gas separation using carbon active bed.

II. CARBON BED VERSUS COAL BED PROPERTIES

[5]Carbonized wood, which can be regarded as a crude form of activated carbon by present-day standards, has been in use for many thousands of years. In about 1500 B.C., the Egyptians, who were aware of the adsorbent properties of wood charcoal. The decolorization and gas-adsorption properties of various carbon products were first investigated in the late nineteenth century, their development having gained impetus from the need for gas adsorbents to protect people against the poisonous gases used in World War I.

What is Activated Carbon? Activated carbon is a generic term for a family of highly porous carbonaceous materials, none of which can be characterized by a structural formula or by chemical analysis. The volume of the pores in activated carbons is generally defined as being greater than 0,2 ml/g, and the internal surface area is generally larger than 400 m^2/g as measured by the nitrogen BET method. The width of the pores varies from 3 Å to several thousand angstroms, and the pores are generally classified for convenience in terms of their diameters such as shown in Table 1. In cross-section, the pores appear to be cylindrical or rectangular in shape, but can also occur in a variety of irregular shapes. Pores may also have constrictions or bottlenecks.

Macropores, which generally contribute very little to the total internal surface area of the product, depend mainly on the nature of the carbonaceous raw material employed and the preliminary manufacturing process, including grinding and agglomeration of the raw material. Their major function is to serve as transport arteries that make the internal parts of the carbon granules readily accessible to the molecules being adsorbed. The transitional pores account for about 5 per cent, and the micropores for about 95 per cent, of the internal surface area. The micropores are largely the product of the activation process.

Structure. X-ray-diffraction studies have shown that the structure of thermally activated carbon is similar to that of graphite. Ideal graphite, depicts in Figure 1, consists of layers of fused hexagons held approximately 3,35 Å apart by Van der Waals forces, so that the carbon atoms in anyone plane lie above the centres of the hexagons in the layer immediately below it.

A brief comparison of carbon bed and coal bed conceptual structure is pointed out in Figure 2. In both cases, gas is stored, at particular pressure, within the matrix by a process known as adsorption. In the process, the gas molecules adhere to the surface of the carbon bed. As the pressure is reduced, gas is released from the surface, diffuses through the matrix and flows through the fracture system.

Characterization of Activated Carbons. The different types of activated carbon can be distinguished from one another only by reference to cer-

Table 1
Activated carbon pores classification[5]

Macropores	500 to 20000 Å
Transitional pores (mesopores)	100 to 500 Å
Micropores	8 to 100 Å

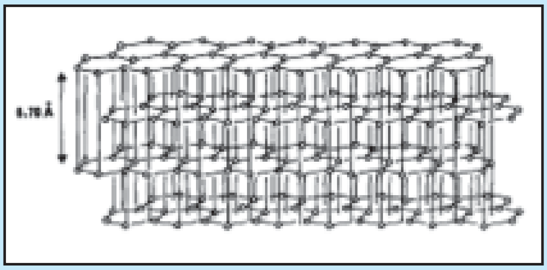

Figure 1
Schematlc representation of the structure of graphite[5]

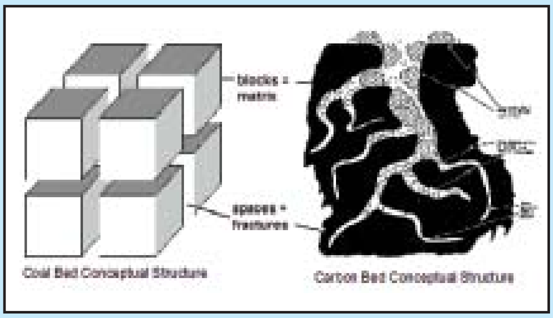

Figure 2
Carbon bed and coal bed conceptual structure[1, 5,9]

tain physical and chemical properties. Important physical properties are the number and size distribution of the pores, bulk density, dry impact hardness, wet abrasion resistance, and particle-size distribution. From the chemical point of view, comparisons are based on the ability of the different products to adsorb various selected substances from the gaseous phase. Coal-based activated-carbon products are characterized by a tridisperse pore-size distribution, i.e. they contain micropores, mesopores, and macropores, as is apparent from Figure 3.

Adsorptive Properties. It is generally conceded that activated carbon owes its adsorptive properties primarily to its large internal surface area, as well as to its pore-size distribution, and that the external surface area and the nature of the surface oxides play minor roles. The size of the pores developed during activation therefore has an important influence on adsorption behaviour because the pores act as a screen. This screen prevents the adsorption of large molecules, but promotes the adsorption of an adsorbate that fits snugly into the pores, making the maximum number of contacts with the adsorbed molecule.

Activated carbon functions by adsorption, i.e. by the adhesion of certain substances to the internal surface constituting the walls of the pores. Hence, the greater the adsorption surface available, the better is the adsorption function. Adsorption occurs as the result of an imbalance of the forces that act upon the carbon atoms constituting the surface of the pore wall. Such an imbalance is inherent in all surfaces and, in an attempt to rectify it, molecules are adsorbed from the gaseous or aqueous phases, and are attracted and held to the surface. Surface adsorption, regardless of the energy of the interaction, must always proceed with a negative change in free energy as well as a decrease in entropy, which result in a negative change in free enthalpy. Hence, adsorption is always an exothermic process.

There are two types of adsorption process: physical and chemical adsorption. Physical adsorption involves weak Van der Waals forces (also dipole-dipole interactions and hydrogen bonding), and the processes are generally reversible. Chemical adsorption refers to processes involving homopolar forces (as in ionic or covalent bonds), and such processes are generally irreversible. Nevertheless, in most instances, the adsorptions can be classified as being physical in nature. In general, the factors that influence the adsorptive behaviour of activated carbon from vapor phases are temperature (adsorption generally decreases with increasing temperature); the pH value of the solution (carbon generally has a low affinity for ions), particularly those with a high charge-to-surface ratio.

Table 2
Carbon Content of Activated carbon raw material[5]

Material	Approximate carbon content, %
Soft wood	40
Hard wood	40
Coconut shell	40
Lignite	60
Bituminous coal	75
Anthracite	90

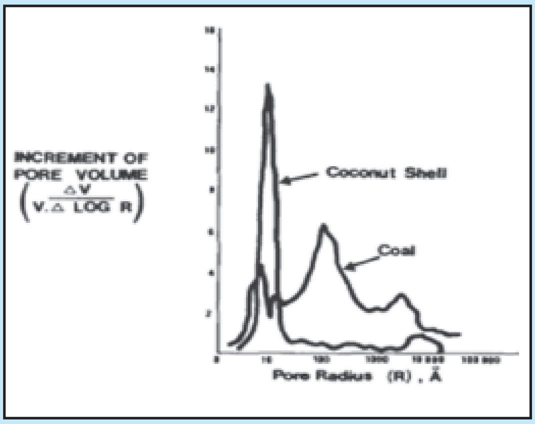

Figure 3
Pore-size distributions for A typical thermally coal-based activated carbon[5]

For molecules to be adsorbed, they must reach the internal surface of the macro pores by diffusion. Therefore, the reaction time will be influenced by the length of the diffusion path, and the kinetics of adsorption will increase with decreasing particle size.

Activated carbon is a very versatile substrate with respect to its interactions with various organic compounds. It is able to function as a simple adsorbent since molecular compounds can be physically adsorbed onto its large internal surface area, and be retained there by forces of the Van der Waals type. The carbon is generally a non-polar material, it adsorbs organic compounds including methane in preference to polar inorganic species.

Raw Materials. Activated carbon can be manufactured from any carbonaceous raw material because of relatively low volatile and high carbon material content. Numerous patents have been granted for processes, to involve the removal of volatile matter from raw materials such as various ranks of coal (peat, lignite, bituminous coal, and anthracite). One of the advantages of bituminous coal and anthracite is their relatively low volatile and high carbon material content (Table 2) and, hence, their high yield of products.

III. VARIABLE PRESSURE WAVE CYCLES CONCEPT

Pressure Wave Cycles concept is developed based on Pressure-swing adsorption - desorption (PSA) technique commonly applies in natural gas separation using carbon active bed. PSA[1] is a cyclic process based on pressure gradients between successive adsorption and desorption runs. This technique is nearly isothermal and it contrasts with the traditional saturation of the adsorbent bed by a stream of gas, followed by thermal desorption. Under favourable conditions, PSA is considered to be developed to model flow rates in carbon bed to represent CBM interflow performance.

In principle, this PSA model development is applied to introduce Variable Pressure Wave Cycles to a hypothetical methane saturated carbon bed to examine interflow behaviour of methane free gas desorbed from meso and micropores of the bed. An evaluation is then conducted to determine the main parameters which play dominant role in the bed interflow performance. In the case of active carbons, the static adsorption of organic vapours or gas can be described successfully within the framework of Dubinin's and Langmuir Isotherm theory. It appears that the dynamics of desorption can be related to various parameters of the Pressure Wave Cycles (PWC) hypothetical system.

Typical schematic view of PSA apparatus[5] which is developed to the PWC hypothetical system is shown in Figure 4. It consists of two parallel columns filled with methane saturated active carbon and working alternatively in the adsorption or in the desorption mode at particular temperature T° K. Cyclic compressed inert gas is flowed to create pressure waves. The compressed inert gas (C) is introduced alternatively into column (1) or (2). After a contact time of several minutes, the gas leaves the column (3). Part of the stream (4) is used to sweep the other column at variable pressures. The gas flowrates and/or pressures can be monitored by appropriate apparatus.

Having been flushed at particular pressure, the column is returned to the adsorption mode and a new batch of the compressed inert gas is introduced. This cyclic process can be repeated a number of times before a breakthrough occurs, depending on the initial concentration, the flow rate, the duration of the adsorption cycle, the adsorption pressure, characteristics of the carbon bed. Under optimum conditions, the PWC hypothetical (PSA based development) system can be used over long periods of time (up to hundreds of cycles), but diffusion through the bed and ageing of the carbon may be the ultimate limitation

The result of previous study for the dynamic desorption of single organic vapor from carbon beds saturated under different conditions can be fitted to the following equation [6]:

$$N_a(t) = N_{ao} \text{ x } (1 - \exp (-(K_c \text{ x } t)^{1/2})) \qquad (1)$$

$$\text{Log } f = 2/7 \text{ x } [2 \text{ x Log } (K_c \text{ x } B_e \text{ x } E_o) - \text{Log } (P_s \text{ x } \theta^4 \text{ x } 4{,}35) + 15] \qquad (2)$$

$$\theta = N_a \text{ x } V_m/W_o \qquad (3)$$

$$E_o = B_e \text{ x } (-RT \text{ x Ln } (K_L/K_o)) \qquad (4)$$

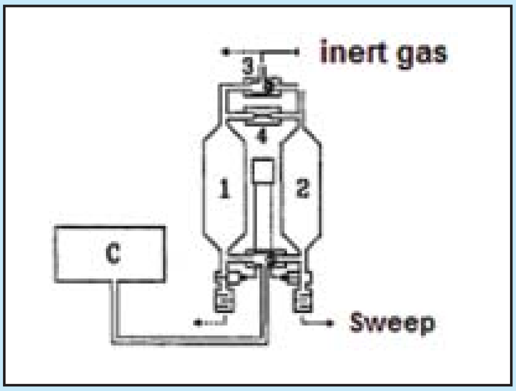

Figure 4
Typical schematic view of PSA apparatus[6]

Table 4
Fixed parameter in use for PWC hypothetical system simulation

[1]Adsorption Energy of CH_4 (E_o)	=	18,835 kJ/mole
Affinity Coefficient of CH_4 (B_e)	=	0,3 (< CO_2 = 0,35)
[2]Carbon bed micropore volume (W_o)	=	0,0008 m^3/Kg
[6]Molar volume of CH_4 (V_m)	=	0,0224000 m^3/mol
Total amount initially CH_4 in the bed (N_a)	=	1 mol/Kg

N_a(t) represents the amount desorbed at time t and N_{ao} is the total amount initially present in the bed. The kinetic constants K_c could be fitted to the empirical relation equation (1) containing the properties of the vapours and the carbon beds, where f is the flow rate (dm^3/min) at which the column is swept at various pressures or 1 atm; q and P_s are the affinity coefficient and the saturation pressure of the organic vapour (at which gas volume adsorb per unit weight of solid) and q represents the degree of micropore filling of the carbon. K_c depends on the average pore width and on the size of the adsorbed molecule. E_o is an inverse function of the average micropore width, and the affinity coefficient q represents the degree of micropore filling of the carbon (N_a/N_{ao}). N_{ao} itself is equal to the micropore volume W_o of the carbon divided by the molar volume V_m of the liquid-like adsorbate. θ increases with the molar volume of the adsorbate.

Table 5
The result of PWC hypothetical system simulation

K_c	P_s, Psi	Flowrate, MMCFD
0,001	200	1,2434
0,0047	210	1,8592
0,008	220	2,0834
0,012	230	2,2555
0,018	240	2,4454
0,025	250	2,5973
0,034	260	2,7455
0,058	270	3,1000
0,097	280	3,4842
0,135	290	3,7197
0,163	300	3,710

IV. PRELIMINARY CARBON BED INTERFLOW PERFORMANCE SIMULATION

A preliminary simulation to find the magnitude of free gas flow rate in carbon bed to represent its interflow performance has been carried out using equation (1) to (5) and data related to carbon bed taken from previous studies such as pointed out in Table 4. Variables in the simulation are kinetic constant K_c and pressure wave hypothetically generated requires to overcome gas saturation in the bed, P_s.

The result of the simulation is shown in Table 5 and Figure 5.

The simulation result shows the trend of improving gas flowrates in the bed due to variable hypothetic pressure waves generated at various kinetics of adsorption/desorption (K_c). However, the improvement is limited to asymptotic flowrate at around 3.7 MMCFD. Continous increase of the pressure leads to an error drop of the flowrate beyond the trend line. This phenomenon seems to follow Langmuir Isotherm theory for the desorption of gas from coal as qualitatively depicted in Figure-6. Langmuir Volume (V_L) is the maximum amount of gas that can be adsorbed on a piece of coal at infinite pressure. This value is asymptotically approached by the isotherm as the pressure increases. Therefore, the improvement of gas flowrate is limited by maximum amount of gas that can be adsorbed in the bed.

V. PARAMETER SENSITIVITY ANALYSIS

Variables in the simulation using equation (1) to (5) are kinetic constant K_c and hypothetic pressure waves generated require to overcome gas saturation in the bed, P_s. Hypothetic pressure waves have been ranged to reflect initial saturation presssure and maximum pressure at which gas volume adsorb per unit weight of carbon bed. While kinetic constant has been considered as a variable to represents the mechanism of single gas adsorption/desorption and potential rate controlling mass transport and any chemical reaction processes.

The simulation results demonstrate the sensitivity of gas interflow performance to the hypothetic pressure waves generated. in the bed. However, this performance improvement is asymptotically limited to maximum amount of gas desorbed from the bed, as well as Langmuir Isotherm pattern applies for gas desorption from coal[1,10].

Moreover, the interflow performance is also sensitive to the gas adsorption/desorption mechanism and factors controlling mass transport in the bed, in which kinetic constant model take a significant role. At this stage, these kinetic models consider to include are the pseudo-first-order equation, pseudo-second-order equation, and intraparticle-diffusion equation.

The pseudo-first-order equation and pseudo-second-order equation were derived based on fluid adsorption capacity at anytime. [3]Both models are described in equation (6) and (7)[3].

$$q_t = q_e \times (1 - \exp(-K_{c1} \times t)) \qquad (6)$$

$$q_t = q_e \times \ (q_e \times K_{c2} \times t)/(1 + q_e \times K_{c2} \times t) \qquad (7)$$

where q_t and q_e (mg/g) the solid phase adsorbate concentration at equilibrium and at time t (min). K_{c1} and K_{c2} is the kinetic constant for the pseudo-first-order model and pseudo-second-order model, respectively.

The kinetic data can also be analyzed by an intra-particle diffusion kinetic model, formulated as equation (8)[3]:

$$q_t = K_{cp} \times t^{1/2} + C \qquad (8)$$

where K_{cp} (mg/g.minute $^{1/2}$) is the intra-particle diffusion rate constant and C is the intercept of the plot q_t of versus $t^{1/2}$. If this linear plot passes through the origin, then K_{cp} is thought to be one factor sensitively controlling the mechanism and mass transport in the bed.

VI. CONCLUSIONS

Having been discussed in term of variables dominantly effect on Variable Pressure Wave Cycles Hypothetical Model, the following points can be concluded :

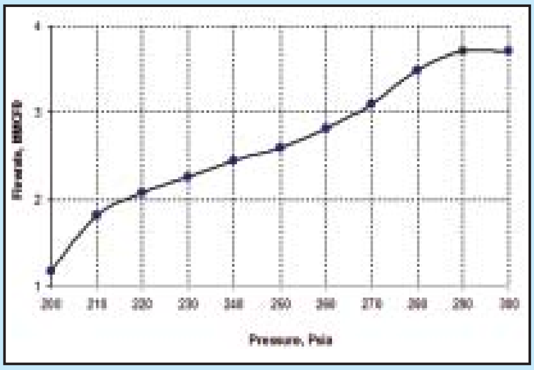

Figure 5
Pressure vs Flowrate for PWC Hypothetical System Simulation

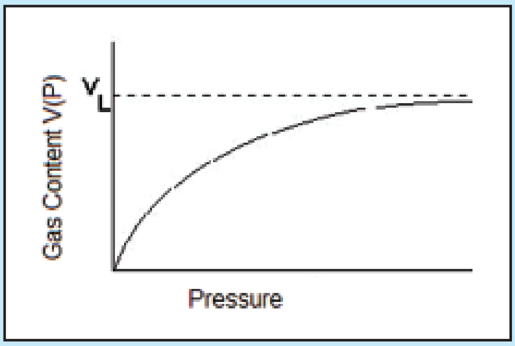

Figure 5
Langmuir isotherm for gas desorption from coal[1]

- Activated carbon bed approach to investigate coal bed characteristics will be acceptable because of the similarities of material properties.
- Variable Pressure Wave Cycles Hypothetical Model demonstrates the possibility of interflow performace improvement in carbon bed.
- The simulation of Variable Pressure Wave Cycles Hypothetical Model shows the sensitivity of gas interflow performance to hypothetic pressure waves generated in the bed. However, this performance improvement is asymptotically limited to maximum amount of gas desorbed from carbon bed.
- Variable Pressure Wave Cycles Hypothetical Model follows Langmuir Isotherm pattern applies for gas desorption from coal.
- It is necessary to further investigate the role of kinetic models as factors controlling adsorption/ desorption mechanism and mass transport to sensitively contribute to the interflow performance in carbon bed.

NOMENCLATURE:

θ : The degree of micropores filling

P_s : the saturation pressure of the organic vapour, atm.

W_o: Micropore Volume, m^3/kg or cm^3/g

V_m: Molar volume of the liquid-like adsorbate, m^3/mol

E_o : Adsorption Energy, kJ/mole = q x heat of adsorption

K_c : Kinetic constants

K_L : Langmuir equilibrium constant

E : Activation Energy of adsorption, J/mol

K_o : Adsorption equilibrium coefficient, L/mg

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