Progress in the Research on Phase Equilibrium of Gas Hydrates in Porous Medium

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Abstract: The obtain of phase equilibrium of gas hydrates are the key factors that estimating the gas hydrate reserves and determining the marine gas hydrate stability zone. For the whole piece of gas hydrate, phase equilibrium conditions measurement and prediction model can’t precisely determining natural conditions of gas hydrate equilibrium factors, currently some scholars in porous medium gas hydrate equilibrium conditions measurement of work, and establish a number of theoretical prediction models. This article goes into particulars the porous medium(especially outburst coal) gas hydrate phase equilibrium conditions measurement and theoretical model for predicting put forward to the future of porous medium gas hydrate phase equilibrium condition of the main direction. We can use the measurement and theoretical model to promote mine gas hydrates formation quickly, which can prevent coal and gas outburst.

Keywords: gas hydrate; phase equilibrium; model; porous media

1. Introduction

Gas hydrates are nonstoichiometric crystalline compounds formed when “guest” molecules of suitable size and shape are incorporated in the well-defined cages in the “host” lattice made up of hydrogen-bonded water molecules. And gas hydrates are also an energy resource composed of natural gas in a solid state, in which water molecules, in a relatively stable composition, surround the gas molecules. These compounds exist in three distinct structure I (sI), structure II (sII), and structure H (sH), which contain differently sized and shaped cages.ThesI and sII hydrates consist of two types of cages, whereas the sH hydrate consists of three types of cages.

It is known that the sediments inhibit hydrate formation and change the stability condition. Capillary inhibition of hydrate stability in narrow pores has been suggested as a possible explanation for differences between the predicted and actual boundary of hydrate stability zones [1].

Coal and Gas outburst, as an extremely complicated geological dynamic phenomenon, caused by coal outburst in a very short time, gas emission is a serious threat to coal mine production safety. China is the world's most serious coal and gas outburst disaster country, outburst mines are more than 2000, accounting for about 22 percent of the total number of mines; at the end of 2008, a total of more than 16,000 prominent, accounting for over 40 percent of the world's total number of outburst accidents. Coal and Gas Outburst accidents not only caused huge loss of people's lives and property, and restricting the development of mining production, which are the major problems to be solved in the mining development of china.

Coal as a sort of porous medium, except for our Task group published 40 related papers of gas hydrate and cured; there are no other researchers’ documents on coal gas hydrate curing reported at present.

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2. Gas Hydrate Phase Equilibrium Conditions Measurement in Porous Medium

For non-methane gas, loose sediment / porous silica and other non-coal a porous medium, some scholars determined the experimental work of the gas hydrate equilibrium conditions, and established a number of theoretical prediction models.

Handa and Stupin[3] first determined under the conditions of 100 ~ 300 K 7nm radius of the porous silica methane - propane hydrate balance rule, found the same temperature, the porous medium pressure gas hydrate equilibrium hydrate equilibrium pressure than the block

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by 20% to 100%. Since then, researchers of all countries determined gas hydrate equilibrium conditions in different porous medium and got a lot of experimental data [4, 5].

Uchida et al.[6,7] found that 10 ~ 50nm in diameter porous glass temperature of methane hydrate decomposition significant downward shift, the temperature deviation is inversely proportional with the diameter, pore depth experimental study shows that the impact on the equilibrium water activity by change induced; Lu et al[8] studied the ultra-fine clay in the fossil methane hydrate stability conditions; Yang et al.[9] Experimental study of the 0.1mm diameter of porous glass in terms of hydrate formation and decomposition of gas hydrate saturation changes and ; Bao-Xiang Wu et al.[10] studied the 272.04 ~ 276.15K, 5.5 ~ 7.5MPa conditions, the water - sediment systems affect the filling rate of methane hydrate in the law of the capillary force mechanism; Anderson et al. [11] for the synthesis of mesoporous silicon pore size distribution and capillary force was hydrate formation conditions and found the role of capillary force hysteresis; unreacted Fan Shuanshi et al. [12,13] Experimental studies 4.5MPa, 274K under the conditions of the porous medium (0.125 ~ 0.300 mm diameter quartz sand) in the formation of gas hydrate phase equilibrium law of the porous medium capillary pressure on the gas - hydrate - Water Phase Equilibrium; Kang et al.[14] measured three kinds of porous silica pore methane - water system Equilibrium conditions of hydrate formation. At the same time, some scholars consider the pore, capillary force distribution and circumstances, the establishment of a number of gas hydrate equilibrium in porous media prediction model.

Clarke et al.[15] In considering the case of capillary pressure in porous media made a prediction of gas hydrate formation conditions in the model, the introduction of gas hydrate in porous media to describe the formation of a new method of phase equilibrium, but ignore the water and hydrates between the surface energy; Wilder et al. [16] the model equation with Clarke and other similar use, but they assume that the interface between the hydrate exists essential difference between the predicted and measured data compared Handa and Stupin greater error, Clarke and Wilder's explanation for this is because the porous media used in experiments is not a single aperture, but there is a distribution, which led to the experimental values and the difference between the calculated values; Yongwon Seo [17] the model taking into account the impact of capillary pressure and porous medium water activity of the reduced expression of the water activity was modified to obtain a porous silica water activity expression; Clennell, Henry, et al. [18,19] based on Gibbs-Thomson equation to establish a marine sediment capillary force under consideration three-phase equilibrium of methane hydrate thermodynamic model; Klauda, Sandler, et al. [20,21] proposed an improved model, and the methane hydrate distribution in marine sediments were predicted; However, Llamedo et al. [22] pointed out that the hydrate formation in porous media and decomposition, the capillary solidified - liquid curvature is not the same, they were accordingly amended, gives the new hydrate - liquid interfacial tension values; Sloan et al. [23] measured an average diameter 55 nm marine sandstones hydrate equilibrium data, analysis of sediment pore capillary force effect on the equilibrium; Yu Xichong et al. [24] derived the hydrate formation in porous media pressure and temperature distributions equation, considering the fluid mechanics in porous media by capillary forces on gas hydrate formation conditions affect; Duan Zhenhao et al. [25] based on van der Waals-Platteeuw model considering the capillary force of marine sediments methane - fluid - Hydration property prediction model thermodynamic parameters of phase equilibrium; Li Xiaosen et al. [26,27] were using two thermodynamic methods (methods based on fugacity equal equal activity-based methods) to predict gas hydrate in porous media with different equilibrium conditions Both methods make use of the van der Waals-Platteeuw model combined with Llamedo other model on the simulation of capillary force.

Wu Qiang et al. [28-30] based on gas hydrates possess advantages of temperate formation conditions, higher gas fraction, larger heat of decomposition, proposed utilizing gas hydrate mechanism of preventing Coal and Gas Outburst new ideas. The technology of main principles : the majority of coal and gas outburst accidents were due to gas occurrence region of disturbances (broken coal or fallen coal) caused by the large amount of gas emission in an instant, therefore, delaying disturbance of gas concentration emission is the effective way to control such accidents ; using the higher gas fraction , larger heat of decomposition properties of gas hydrates, adopting the method of medium and high pressurized water injection and added promoter agent (surfactant and crystal seed etc., its main function is to improve gas hydrate curing thermodynamic condition and control kinetics process of gas hydrate curing) to the water was beneficial to hydrate formation, so that most of the coal seam gas hydrate cure of hydrate formation, thus significantly lower coal seam occurrence of gas pressure ; when excavation work exposing coal seam due to solid gas hydrate dissociation need to absorb a large number of calories,coal seam surrounding rocks coefficient smaller, so the solid gas hydrates could be difficult to melt and decompose in a moment then formed high - pressure gas flow when breaking coal, so as to achieve the purpose of preventing coal and gas outburst.

We (2004-2008) carried out the basic research on gas hydrate material characteristics and formation change regulations, influence mechanism promoters(surfactant and Seeding), initially acquired a typical mine gas hydrate curing law, select a valid improve the conditions for gas hydrate curing thermodynamics and kinetics of partial accelerator types and proportions. In addition, a series of research experiments were conducted to the law of coal - bearing system of gas hydrate curing [31], studied 14.3 ~ 25.4℃ 18.66 ~ 26.70MPa under the condition of coal - surfactant solution systems of gas hydrate formation process and achieved relation curve of pressure - temperature - time on formation process, initially discovered that the existence of porous media(coal)have influence on hydrate formation process.

We carried out a series of experiments on the coal conditions of gas hydrate formation thermodynamics, synthesis of gas hydrates (Figure 1) in coal - surfactant system, initially obtained the datas of coal seam gas hydrate formation temperature and pressure, we found that existence of coal (porous medium) had delaying effects on gas hydrate formation thermodynamics conditions.

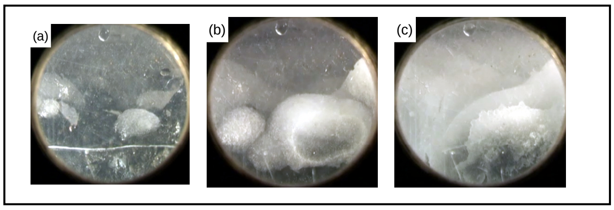

Figure.1. Typical photos of gas hydrate formation in coal - surfactant system at different time (a) 0 min, (b) 13 min, (c) 40 min

3. Prediction Model of Porous Medium Gas Hydrate Phase Equilibrium Conditions

At present, almost all of the thermodynamic models for the prediction of hydrate formation conditions on the basis of the classical statistical thermodynamics, the most successful one was based on the classical model of adsorption theory that put forward by Van der Waals and Platteeuw (1959)， Later the whole piece of gas hydrate in porous medium gas hydrate and most of the theoretical model on this basis. Platteeuw and Van der Waals models, Documents [32, 33] described in detail and will not repeat them here.

Solid Solution in accordance with the theory of gas hydrate stable condition directly depends on the activity of water. Activity decreases, a given temperature hydrate formation increased pressure or pressure hydrate formation temperature decrease. Experimental proof in micro - pore water freezing point is distinctly lower by Handa and Stupin [34] (1992), while propane gas hydrates in porous media of methane decomposition pressure higher than that of the whole piece of gas hydrate decomposition pressure [3]. Therefore, the size limit will lead to water activity lowering; this is similar to inhibitors in the system.

In order to predict phase equilibrium conditions of the gas hydrate in porous medium, on the basis of Van der Waals-Platteeuw model (the size effect was included in the water activity expression), some academics established gas hydrate phase equilibrium prediction models in porous medium.

3.1 Calaque et al. Model (1999)

Clarke et al. [15] believes in porous medium gas hydrate dissociation depending on the conditions of rock and fluid properties, such as wet angle and pore radius. Capillary force of diameter lowers water activity, resulting in diameter in the depression of freezing point of water. They will take surface tension into account, the introduction of a new method of describing porous medium gas hydrate. In the course of their models, suppose with silica gel surface water or ice. Young-Laplace equation determined pressure difference between water and gas phase through using sphere of contact surface.

$$\Delta P = P_g - P_w = \frac{2\sigma_{gw}}{R_p}\cos\theta \qquad (1)$$

Where P_g is the pressure of the gas phase, P_w is the pressure of the water phase; σ_{gw} is the surface tension between water and gas, 71mJ/m2; R_p is the average pore radius; θ is the contact angle with water and silica gel.

Water activity can be written to

$$\ln \alpha_w = \ln\left(\frac{f_w}{f_w^0}\right) = \ln\left(x_w + \gamma_w\right) + \frac{V_w}{RT}\left(-\Delta P\right) \qquad (2)$$

Where α_w is the Water activity, f_w^0 is the fugacity of pure water; f_w is the Porous phase fugacity of water; x_w is the mole fraction of water; γ_w is the Activity coefficient of water; R is the gas constant; T is the temperature; ΔP is given by (1).

In their analysis, they overlooked the surface energy between water and hydrate, due to lowering the freezing point of porous water, the reference temperature is 276.5K.

3.2 Wilder et al. Model (2001)

Wilder et al. [16] consider obviously capillary pressure that caused by interface curvature effect of the water and hydrate in keyhole (and /or water and gas), assumes porous formation of hydrate, a massive water and gas in a state of balance, giving chemical potential difference between the empty hydrate crystal cave and pure water

$$\left(\Delta\mu_w\right)_{pore} = \left(\Delta\mu_w\right)_{bulk} + V_L \frac{2\cos(\theta)\sigma_{hw}}{r} \qquad (3)$$

Where V_L is the water molar volume in pure water, θ is the wet out angle between the pure water phase and hydrate; σ_{hw} is the interfacial tension between water and hydrate Phase; r is the aperture radius.

This point is that Clarke et al. are using the equation model using surface with the Wilder et al. alike, but their assumption of hydrate interface are different in nature.

3.3 Yongwon Seo et al. Model (2002)

Yongwon Seo et al. [38] model considering the effect of capillarity and the lowering of water activity in porous media, amendments to the water activity expression, gives porous silica gel water activity expression

$$\ln a_w = \ln\left(X_w \gamma_w\right) - \frac{V_L 2\cos\theta\sigma_{hw}}{rRT} \quad (4)$$

where V_L is the water molar volume in pure water, θ is the wet out angle between the pure water phase and hydrate; σ_{hw} is the surface tension between hydrate phase and liquid water phase; r is the pore radius.

3.4 Klauda and Sandler Model (2001, 2003)

Klauda and Sandler [20] believed that the laboratory prediction theory model of gas hydrate in porous medium should include pore size distribution; in fugacity models using surface tension between the hydrate and liquid water. They [21] had set up natural gas hydrate phase equilibrium model in the sediments of porous media. They assume that in the process of crystallization and hydrate convex spherical continued to pores. Therefore, the pores of a radius r, hydrated phase pressure is higher than static pressure of the whole piece of hydrate.

$$\mathrm{P}_{\mathrm{pore}}^{\mathrm{r}}\left(\mathrm{r}\right)=\mathrm{P}_{\mathrm{hydro}} - \frac{\zeta_{hl}\sigma_{hl}}{r}\cos\theta_{HL} \quad (5)$$

Where : ζ is the form factors ; σ is the surface tension ; θ is the contact angle of hydrate and liquid water interface, as the contact area for convex ,therefore more than 90°.

As there is no experimental data of surface tension between liquid water and hydrate, therefore assume that it is twice the ice water surface tension. Natural seabed sediment porosity had distribution range, so the average pressure for gas hydrates phase

$$\bar{\mathrm{P}}_{\mathrm{pore}}\left(\mathrm{r}\right) = \mathrm{P}_{\mathrm{hydro}} - \int_0^\infty \frac{\zeta_{HL}\sigma_{HL}}{r}\cos\theta_{HL}\varphi\left(r\right)dr \quad (6)$$

Where φ(r) is the probability density distribution functions of pore size, they assumed it as normal distribution.

$$\varphi\left(r\right) = \frac{1}{\sqrt{2\pi}}\exp\left(\frac{\left(r-R_P\right)^2}{2sd^2}\right), z = \frac{r-R_P}{sd} \quad (7)$$

Where R_P is the average pore radius; sd is the pore size standard deviation; z is the radial distance.

On this basis, they established the fugacity models.

$$f_w^L\left(T,\mathrm{R}_{\mathrm{hydro}}\right) = x_w\left(\mathrm{T},\mathrm{P}_{\mathrm{hydro}}\right)\gamma_w\left(x_w,T\right)P_w^{sat,L}\Delta\exp\left[\frac{V_w^L\left(\mathrm{T},\mathrm{P}_{\mathrm{hydro}}\right)\left(\mathrm{P}_{\mathrm{hydro}} - P_w^{sat,L}\left(T\right)\right)}{RT}\right] \quad (8)$$

4. Conclusions

The article reviews on the study of the experimental and theoretical model of gas hydrate phase equilibrium conditions in porous media. The author argues that future research direction of porous medium gas hydrate phase equilibrium mainly in the following aspects.

Equilibrium conditions measurement of gas hydrate in porous medium to complex system ,the complex system including : mixed aqueous electrolyte solutions in porous media, simple salt and alcohol aqueous solution in porous media ; mixed salt aqueous and alcohol aqueous solution in porous media ; mixed salt and mixed alcohols aqueous solution in porous medium system of natural gas. On the basis of measurement and theoretical model of gas hydrate equilibrium conditions in porous medium, obtaining the balance conditions of natural gas hydrate in nature. And outburst coal gas hydrate curing determination of the law of equilibrium thermodynamics and capillary force is a new problem to be solved.

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