



EXPERIMENTAL AND KINETIC STUDIES ON THE IMPROVEMENT OF SHRINKAGE BUBBLE FORMATION OF GAS HYDRATE

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ABSTRACT

On the base of some kinetics model analysis and kinetic observation of hydrate formation process, a new prediction model of gas hydrate formation is proposed. The analysis of the present model shows that the formation of gas hydrate not only relevant with gas composition and free water content but also relevant with temperature and pressure. Through contrast experiment, the predicted result of the new prediction method of gas hydrate crystallization kinetics is close to measured result, it means that the prediction method can reflect the hydrate crystallization accurately.

I. INTRODUCTION

During the exploitation process, the gas well sometimes closed because of plugging in wellbore or surface pipeline which is caused by gas hydrate [1-4]. In order to solve a series of plugging problems caused by hydrate in oil field and develop natural gas hydrate resources more effectively and utilize hydrate technology more reasonably, the research on natural gas hydrate crystallization kinetics mechanism becomes very necessary [5, 6]. An operation step of crystal nucleus growth process is an important factor need to research in the study of crystallization kinetics [7]. In different system, many factors can be used to control crystal nucleus growth process, such as diffusion, heat transfer, stirring rate, reaction kinetics, and heat exchange rate on surface of crystal. In view of the above factors, many researchers propose the crystallization kinetics model which describes the nucleation based on mass transfer theory, crystallization theory, and two-film gas-liquid mass transfer theory. The generation of hydrate is actually the nucleation and crystal growth process. Kinetics of hydrate formation is related to generation rate, pressure, temperature, and so forth. The process can be clearly divided into three steps: at first the generation of crystal nucleus with critical radius, then solid crystal nucleus growth, and at last the components transfer to solid-liquid interface of nuclear at aggregation state.

Many factors affect the generation of natural gas hydrate; there are three main points. (1) When the gas temperature is equal to or lower than the water dew point and is accompanied with free water or liquid water, then hydrate formed. (2) In condition of certain pressure and gas composition, the temperature is lower than the hydrate formation temperature; then hydrate formed. (3) The high operating pressure will rise the hydrate formation temperature. This paper developed a new prediction method of gas hydrate crystallization kinetics according to the shrinkage bubble model and considering the variation of pressure with time at the same time, to establish a new method for the prediction of natural gas hydrate.

II. MODEL

2.1 Hydrate Growth Dynamic

During the hydrate formation process there is transfer phenomena in the hydrate-gas-water. The kinetic observation of hydrate formation process is shown in Figure 1. From the figure we can know that at first hydrate mainly gathered at the air-water interface layer; when the temperature is lower than the hydrate phase equilibrium temperature, hydrate nucleation formed quickly by gas and water molecules inside the bubble. The generation process of crystal nucleus is the process that water diffuse into a bubble and gas in bubble diffuse out of bubble; finally the bubble in hydrate gradually reduced and even disappeared then hydrate crystals formed. Experiments show that the hydrate formation process is controlled by the transmission rate of gas and water molecules, through the establishment of hydrate formation kinetics method can describe the generation process.



Fig: 1 Kinetic Observation of Hydrate Formation Process

2.2 Shrinkage Bubble Kinetics

Through the hydrate growth kinetic observation we can know that during the growth process of hydrate crystals the bubbles transform into hydrate; the process is shown in Figure 2. In Figure 2, the exterior is water, the internal is gas, and the ring is hydrate.

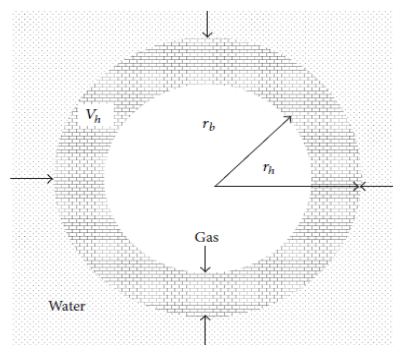


Fig: 2 Process of bubble transforming into Hydrate

Hydrate volume in hydrate crystals is

$$V_h = \frac{4}{3}\pi(r_h^3 - r_b^3)$$

Where r_h is outer radius of hydrate, r_b is bubble radius, and V_h is hydrate volume in hydrate crystals.

The growth rate of hydrate is

$$\frac{dV_h}{dt} = 4\pi[r_h^2 \frac{dr_h}{dt} - r_b^2 \frac{dr_b}{dt}]$$



During the formation process of hydrates, the chemical potential in phase equilibrium systemization is equal. According to gas adsorption model and the law of diffusion, the hydrate formation rate equation is obtained as follows

$$\frac{dV_h}{dt} = 4\pi D \frac{r_b r_h}{r_h - r_b} \left[\frac{p_b - p_d}{p_b} \right]$$

Where p_b inner air is pressure of bubble and is p_d decomposition pressure. D is the mass transfer coefficient and it can be expressed as

$$D = \frac{(1 - y_d) D_{ha}}{y_d} + v c_d D_{hw}$$

Where y_d is lattice occupancy, v is vacant hole numbers of each water molecule, c_d is water solution concentration under the decomposition pressure of hydrate, D_{ha} is mass transfer coefficient between hydrate and gas, and D_{hw} is mass transfer coefficient between hydrate and water.

Supposing the gas in bubble and hydrate is ideal gas, then

$$v_b p_b + v_h p_{ha} \phi = v_{bo} p_{bo}$$

Where ϕ is porosity and v_b is bubble volume. p_{ha} is the pressure when the gas density in bubble is equal to the gas density in hydrate,

Which can be expressed as

$$p_{ha} = \frac{\rho_{ha} R_g T}{M}$$

Because the reaction is controlled by mass transfer, so the change rate of hydrate volume is

$$w_h = - \frac{\left[\frac{dV_b}{dt} + (1 - d_{ha}) \left(\frac{dV_b}{dt} \right) \right]}{(V_b + V_h)}$$

From the experiment we can know that hydrate is plastic materials, so

$$p_1 - p_b = \frac{4}{3} K_c (\omega - c\omega),$$

Where is compressibility of vacant hole.

Then forward formula becomes

$$p_1 - p_b = \frac{4}{3} K_c w_h \left[\frac{r_h^3 - r_b^3}{r_h^3} \right],$$

$$\frac{dV_b}{dt} = - \left[\frac{V_b}{p_b} \frac{dp_b}{dt} + \frac{p_{ha} \phi}{p_b} \frac{dV_h}{dt} \right]$$

By comprehensive analysis

$$r_h = \left[\frac{3(V_{bo} p_{bo} + r_b^3)}{4\pi p_{ha} \phi} \right]^{1/3}$$

Through shrinkage bubble kinetics model the relationship between inner air pressure of bubble, outer radius of hydrate, bubble radius, and time can be known. But in the actual conditions, only environmental pressure can be

detected, so it is necessary to consider relationship between environmental pressure and time to improve the shrinkage bubble kinetics.

2.3 Improvement of Shrinkage Bubble Kinetics Model

According to the constant volume substance equilibrium rule the alternation law of pressure with time can be known. In the experiments, the volume is constant which is equal to the volume of natural gas and water before hydrate formation and equal to the volume of residual gas, water, and hydrate after hydrate formation; then the pressure change. The process is shown in Figure 3.

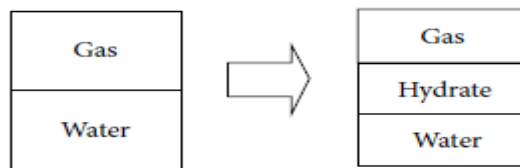


Figure:3 Chart of Hydrate Preparation

According to the principle of material balance, before hydrate formation there are

$$V_{sum} = V_g + V_w,$$

$$V_g = \frac{ZT p_{sc} V_{gsc}}{\rho_1 T_{sc}},$$

$$V_w = B_w V_{wsc},$$

Where v_g is gas volume in the vessel, m^3 . v_w is water volume in the vessel, m^3 . Z is Z-factor at the vessel pressure, dimensionless. T is temperature in vessel, K. p_1 is the pressure in vessel before hydrate formation, MPa. T_{sc} is the temperature at standard state, K. p_{sc} is the pressure at standard state, MPa. v_{gsc} is the injected gas volume at standard state, m^3 . v_{wsc} is the injected water volume at standard state, m^3 . B_w is the volume coefficient of water, dimensionless.

After hydration formation there are

$$V_{sum} = V'_g + V'_w + V_h,$$

$$V'_w = V_w - V_{wc},$$

$$p_2 = \frac{N_h R Z T}{V_{sum} - V'_w - V_h},$$



$$V_{wc} = \frac{KN_h}{M_w \rho_w}$$

$$N_h = \frac{V_h \rho_h}{M_h}$$

$$V_h = n v_h,$$

$$n \leq \frac{S_{GW}}{\pi \left(\frac{8v_h}{4\pi} \right)^{\frac{2}{3}}},$$

REFERENCES

- [1] E. D. Sloan, *Hydrate Engineering*, Society of Petroleum Engineers, Richardson, Tex, USA, 2000.
- [2] I. U. R. F. Makogon, *Hydrates of Hydrocarbons*, Pennwell Books, 1997.
- [3] X.-H. Tan, X.-P. Li, and J.-Y. Liu, "Model of continuous liquid removal from gas wells by droplet diameter estimation," *Journal of Natural Gas Science and Engineering*, vol. 15, pp. 8–13, 2013.
- [4] X.-H. Tan, J.-Y. Liu, X.-P. Li, G.-D. Zhang, and C. Tang, "A fractal model for the maximum droplet diameter in gas-liquid mist flow," *Mathematical Problems in Engineering*, vol. 2013, Article ID 532638, 6 pages, 2013.
- [5] J. Cai, E. Perfect, C.-L. Cheng, and X. Hu, "Generalized modeling of spontaneous imbibition based on hagen-poiseuille flow in tortuous capillaries with variably shaped apertures," *Langmuir*, vol. 30, no. 18, pp. 5142–5151, 2014.
- [6] X.-H. Tan, X.-P. Li, J.-Y. Liu, G.-D. Zhang, and L.-H. Zhang, "Analysis of permeability for transient two-phase flow in fractal porous media," *Journal of Applied Physics*, vol. 115, no. 11, Article ID 113502, 2014.
- [7] E. D. Sloan Jr. and C. Koh, *Clathrate Hydrates of Natural Gases*, CRC Press, New York, NY, USA, 2007.