RESISTANCE STUDY ON METHANE HYDRATE DISTRIBUTION IN QUARTZ SAND AND EXCESS WATER

Juan He^{1,2,4}, Xiaosen Li^{1,2,3}, Zhaoyang Chen^{1,2,3*}, Yu Zhang^{1,2,3}, Zhiming Xia^{1,2,3}, Kefeng Yan^{1,2,3}

1 Key Laboratory of Renewable Energy and Gas Hydrate, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, P. R. China.

2 Guangzhou Center for Gas Hydrate Research, Chinese Academy of Sciences, Guangzhou 510640, P. R. China.

3 Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou 510640, PR China.

4 University of Chinese Academy of Sciences, Beijing 100049, PR China.

Abstract

Hydrate distribution controls the properties of hydrate-bearing sediments. Few methods cannot be available to understand hydrate distribution characteristics macroscopically at present. Designing a large-scaled pressure vessel possessing five measuring positions, we investigated hydrate distributions through the features of resistances in quartz sands and excess water. The results show that gas and hydrate governed the characteristics of resistances during hydrate formation stage. Different increasing fluctuations of resistances can show hydrate distributions. In our experiment, hydrates were considered to mainly distribute in the middle of horizontal artificial sediments. The resistances of hydrate-bearing sediments may offer a reference to hydrate distributions.

Keywords: resistance, hydrate formation, non-uniform distribution, excess-water

1. Introduction

At present, methane hydrate has been deemed as one of potential energy resources. Many researches and field tests have been conducted to achieve commercial production technologies for hydrate development. In these works, synthetic hydrate samples are widely used to investigate the properties of hydrate-bearing sediments such as permeability, thermal conductivity, and so on, which provides basic messages for numerical simulations. The process of hydrate formation by excess-water method in the laboratory is similar to the circumstance in actual hydrate reservoirs, so it is used widely. But using this method can lead to non-uniform distribution of hydrate in artificial sediments, which has been observed microscopically via X-ray computed tomography (CT) [1-5]. However, there are rarely reports about judging hydrate distribution from macro-scales. This situation brings about uncertainty to experiments.

Resistivity, resistance, or impendence represents electrical properties of hydrate-bearing sediment. Although they are governed by ion concentrations, some other factors have been proven to affect electrical properties. No matter CO₂ hydrate, CH₄ hydrate, or THF hydrate in porous medium, with increasing temperature, bine concentration, and water content, resistivity or resistance would diminish [6-8]. Yet the correlation between hydrate saturation and resistivity or resistance seems unclear. As some literatures reported, the resistivity was not always increased when hydrate saturation increased in artificial hydrate specimens, owing to Oswald ripening [9-11]. On the other hand, these electrical properties were used to study hydrate formation and dissociation in artificial specimens. Resistant would increase during the formation, while it deceased dramatically in dissociation phase [12-15], due to ionic concentration changes. The "blockage" mechanism of hydrate was assumed as contribution to increasing resistivity in the formation stage. Under excess-water hydrate formation environment, hydrate in large pores and throats can be assumed as a key

factor to affect the electrical properties during hydrate formation. In addition, gas would also hinder ions to flow, so gas also can be not negligible. These characteristics benefit us to judge the hydrate distribution.

Hence, in order to understand hydrate distribution macroscopically, excess-water method was used to form hydrate with different saturations in a pressure vessel with different electrical measuring locations. The resistance changes were employed to study hydrate contents in different places during hydrate formation.

2. Experiments

2.1 Apparatus and materials

Figure 1 is the schematic of apparatus employed to measure electrical features of methane hydrate-bearing porous media. The pressure vessel is a cylinder and capable of withstanding a maximum pressure of 33.0 MPa. The inner dimensions of the vessel are 100 mm in diameter and 700 mm in length. The internal bulk volume of it was measured as 5.701 L through water injection. Twenty thermocouples are inserted in the vessel for temperature measurement during hydrate formation phase. The thermocouples are numbered from 1 to 20. The electrode encompasses two probes. The vertical and horizontal distances between them are 90 mm and 10mm, respectively. Five electrodes are arranged at a distance of 50 mm, 200 mm, 350 mm, 500 mm, and 650 mm respectively from the left of the vessel. They are labeled as R1, R2, R3, R4, and R5. Two pressure transducers with maximum ranges of 40 MPa are fixed on inlet and outlet of the vessel, respectively. A gas tank with volume of 4.0 L is used to store methane of a certain pressure. In order to reduce the effect of temperature on measurements, a container with volume of 11.0 L is to provide cool water with a temperature needed for experiments. A data acquisition of Agilent logs data, and a computer records all data.

In our experiments, quartz sand with 100-120 mesh was chosen as porous media. Deionized water with a resistivity of 18.25 M Ω /cm was prepared by an ultrapure water meter. Methane gas with the purity of 99.99% was supplied by the Foshan Kody Gas Chemical industry, Co., Ltd., China.



Figure 1 Experimental schematic of apparatus for resistance measurements

2.2 Experimental process of Hydrate formation

The excess-water method was used to prepare hydrate samples, and the experimental processes are as follows: (1) after filled with dry quartz sand, the pressure vessel was immersed into the temperature controlled water bath with 281.15 K. The back pressure valve was set in 13 MPa. Deionized water with 281.15 K was injected into the vessel with injection rate of 5 ml/min until a constant flow rate in the outlet. The porosity of quartz sand was measured at 48.24%. The pressure of vessel was remained this condition for about three hours. In this period, resistances were metered as a start point. When resistance values held steady, a relatively constant condition was achieved in the vessel. (2) The vent valve (Figure 1) was opened, and a predetermined amount of water was driven out by gas injection. During this period, gas should not be displaced out. After the water displacement finished, the vent valve was shut down. (3) The vessel was pressurized to a given value with methane gas and deionized water, respectively. (4) The system was maintained for a few

days to allow the hydrate formation. The pressure, temperature, and resistance data were recorded at 60

3. Results and discussion

Figure 2 is the changing resistances in whole process of hydrate formation whose hydrate saturation is 15.50%. This process was divided into five stages. After the resistances of five positions had become steady at the stage 1, partly water was displaced out by gas injection repeatedly. During the stage 2, the increasing resistances in five positions were observed outstandingly. The gas gradually entered larger pores and throats and thus governed the changes of resistances. Afterwards, gas injection increased the pressure of the vessel from 11.75 MPa to 17.80 MPa at the stage 3. And the pressure of the vessel further varied from 17.80 MPa to 24.3 MPa through water injection. Since the time of both stages last shortly, there were a little changes in resistances of five measuring points. The gas and the water were regarded as key influencing factors in the stage 3 and 4, respectively. At the stage 5, with deceasing pressure in the vessel, the gas in quartz sands was gradually forming hydrates. Before the first water injection, all measuring positions had tendencies featured with different increasing degrees. But when the water was added to the vessel in the first time, all of resistances scaled down. The residual gas was s time interval during hydrate formation phase.

intended to synthetize more hydrates. However, the resistances in five positions almost had little changes after the second water injection was performed. This show that there were not much new formed hydrates causing the reduction of ion concentration in these five positions. Meanwhile, the second water injection had little effects on resistances of five positions, so the water may not be an important factor. The remaining gas and methane hydrate should control the features of resistances in the stage 5.

Hydrate distributions related to local hydrate contents closely. This hydrate content can affect the changes of resistances in five positions. Therefore, these changes of resistances can be used to analyze hydrate distributions in the quartz sands. From the stage 5 in the Figure 2, compared with the measuring position R1 and R5, the position R2 to R4 possessed the larger increasing fluctuations of resistances. Hence, these places had more gas to form hydrates. And different measuring points had various local hydrate contents, though they are under the same hydrate saturation. In our experiment, hydrates were mainly distributed in the middle of the vessel. This indicates hydrate distributions were non-uniform via using excess-water method [16].



Figure 2 Characteristics of the resistances in the process of hydrate formation (S_h =15.50%)

4. Conclusions

Electrical properties of hydrate-bearing quartz sand were measured and investigated during hydrate formation in this work.

(1) The gas and the hydrate governed the characteristics of resistances in different measuring points during hydrate formation stage.

(2) More hydrates would bring larger increasing fluctuations of resistances.

(3) Hydrates were distributed non-uniformly in the vessel.

ACKNOWLEDGEMENT

The authors are very grateful for the support of the National Natural Science Foundation of China (51576202 and 51736009), the National Key R&D Program of China (No.2016YFC0304002), the Special Project for Marine Economy Development of Guangdong Province (GDME-2018D002) and the CAS Science and Technology Apparatus Development Program (YZ201619), which are gratefully acknowledged.

Reference

[1] Wang J-Q, Zhao J-F, Yang M-J, Li Y-H, Liu W-G, Song Y-C. Permeability of laboratory-formed porous media containing methane hydrate: Observations using X-ray computed tomography and simulations with pore network models. Fuel. 2015;145:170-9.

[2] Tohidi B, Anderson R, Clennell MB, Burgass RW, Biderkab AB. Visual observation of gas-hydrate formation and dissociation in synthetic porous media by means of glass micromodels. Geology. 2001;29.

[3] Konno Y, Jin Y, Uchiumi T, Nagao J. Multiple-pressure-tapped core holder combined with X-ray computed tomography scanning for gas-water permeability measurements of methane-hydrate-bearing sediments. Rev Sci Instrum. 2013;84:064501.

 [4] Kerkar PB, Horvat K, Jones KW, Mahajan D. Imaging methane hydrates growth dynamics in porous media using synchrotron X-ray computed microtomography.
Geochemistry, Geophysics, Geosystems. 2014;15:4759-68.

[5] Chaouachi M, Falenty A, Sell K, Enzmann F, Kersten M, Haberthür D, et al. Microstructural evolution of gas hydrates in sedimentary matrices observed with synchrotron X-ray computed tomographic microscopy. Geochemistry, Geophysics, Geosystems. 2015;16:1711-22.

[6] B. A. Buffett OYZ. Formation of gas hydrate from dissolved gas in natural porous media. Marine Geology. 2000;164:69-77.

[7] Li F-G, Sun C-Y, Li S-L, Chen G-J, Guo X-Q, Yang L-Y, et al. Experimental Studies on the Evolvement of Electrical Resistivity during Methane Hydrate Formation in Sediments. Energy & Fuels. 2012;26:6210-7.

[8] Pearson C, Murphy J, Hermes R. Acoustic and resistivity measurements on rock samples containing tetrahydrofuran hydrates: Laboratory analogues to natural gas hydrate deposits. Journal of Geophysical Research. 1986;91:132-8.

[9] Lee JY, Santamarina JC, Ruppel C. Parametric study of the physical properties of hydrate-bearing sand, silt, and clay sediments: 1. Electromagnetic properties. Journal of Geophysical Research. 2010;115.

[10] Ren SR, Liu Y, Liu Y, Zhang W. Acoustic velocity and electrical resistance of hydrate bearing sediments. Journal of Petroleum Science and Engineering. 2010;70:52-6.

[11] Spangenberg E, Priegnitz M, Heeschen K, Schicks JM. Are Laboratory-Formed Hydrate-Bearing Systems Analogous to Those in Nature? Journal of Chemical & Engineering Data. 2014;60:258-68.

[12] Chen Q, Diao S, Ye Y. Detecting Hydrate in Porous Media Using Electrical Resistance. Natural Gas Hydrates2013. p. 127-40.

[13] Li SX, Xia X, Xuan J, Liu YP, Li QP. Resistivity in Formation and Decomposition of Natural Gas Hydrate in Porous Medium. Chinese Journal of Chemical Engineering,. 2010;18:39-42.

[14] Priegnitz M, Thaler J, Spangenberg E, Schicks JM, Schrötter J, Abendroth S. Characterizing electrical properties and permeability changes of hydrate bearing sediments using ERT data. Geophysical Journal International. 2015;202:1599-612.

[15] Zhou X, Fan S, Liang D, Wang D, Huang N. Use of Electrical Resistance to Detect the Formation and Decomposition of Methane Hydrate. Journal of Natural Gas Chemistry. 2007;16:399-403.

[16] Timothy J. Kneafsey YS, Arvind Gupta, Liviu Tomutsa.
Permeability of Laboratory-Formed
Methane-Hydrate-Bearing Sand: Measurements and
Observations Using X-Ray Computed Tomograph. SPE
Journal. 2011:78-94.