A New Classification and Description of Shale Pore System: from the Burial History Perspective

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Abstract. Accurate micro-storage and mechanism of shale gas is important for defining and describing the adsorption characteristics, and for gas-in-place estimation. In this paper, reservoir forming process is divided into early stage and late stage, and the initial gas-water distribution in different stage is redefined. Different from the widely used solid-gas interface adsorption theory, the pore system in original shale reservoir is divided into solid-gas system and solid-liquid-gas system. Gas pores existing in organic matters belong to solid-gas system, and are classified into residual gas pores and metamorphic gas pores. Plant tissue pores in organic and mineral pores belong to solid-liquid-gas system. Their characteristics are described.

1. Introduction

Although shale gas is now considered to be an increasingly important source of natural gas worldwide, some problems do exist during the process of shale gas. Some studies pointed to high rates of decline of some shale gas wells as an indication that shale gas production may ultimately be much lower than is currently projected. This might be because the accumulation and storage mechanism of shale gas reservoirs are not fully understood. Accurate classification and description of shale pore system is important for defining and describing the adsorption characteristics and reserve prediction.

Studies shows that Shale reservoirs usually have certain water saturation, 7~20% for Haynesville, 25~35% for Barnett, 15~35% for Marcellus and even 42% for Eagle Ford[1,2]. Different from inorganic pore systems, organic pore systems in shales are hydrocarbon-wetting in traditional view. However, recent experimental studies have proven the existence of water content in kerogen material. Ruppert et al[3] pointed out that Barnett shale pores had the access to both methane and water over a wide size range (10 nm to 10 μm) and surprisingly the fine pores (<30 nm) appeared to be much more accessible to water than methane. Also, Yinan Hu et al [4] studied the interaction between water and hydrocarbon though molecular dynamics, finding that kerogen may have mixed-wet or even hydrophilic characteristics. Although the studies of water sorption have been studied for decades, such as on carbon nanotubes, graphene, coals, the water content associated with shales is a relatively new research direction to understand shales.

In this study, the generation, dissolution, adsorption and migration of methane is described in micro-scale during the reservoir forming process. Pore system in shales is divided into two categories from the point of liquid-gas distribution: solid-gas system and solid-liquid-gas system. Their types,
sizes and shapes are described, respectively. This study proposes a new classification of the shale pore system, which can provide a better understanding of the adsorption mechanism of shale reservoirs.

2. Characteristics of shale gas reservoir

2.1. Reservoir forming process

Most current shale-gas reservoirs could have been deposited in the marine environment like lakes (lacustrine), deeper water basins, or in associated swamps and mires along the margins of lakes or seas [5]. For example, the Barnett strata, which is a classic shale-gas system, were deposited in a deep water foreland basin that had poor circulation with the open ocean[6]. During the process of sedimentation and diagenesis, loose rock pore has been compacted. Large amount of formation water contains is discharged, and pore volume decreased. In hydrocarbon-generation process, large amount of shale gas gathered forming an abnormal high pressure inside reserve because of huge, thick overlying strata. When this pressure exceeds the fracturing pressure of overlying strata massive micro-crack forms, it provides channels for water and gas discharged outwards. After the water-gas discharged process, pressure inside the formation declines and the micro-fractures tend to close. These repeating processes make the liquid water less and less. Clay minerals of shale are hydrophilic, making inorganic pores surrounded by water molecules or movable water, which dissolved only a few amounts of methane molecules. Water that trapped in inorganic pores cannot be fully transported during hydrocarbons generating and gas output stage of kerogen. The content of clay minerals in shales is much higher than that in coals by nearly 30%~50% [7]. How the adsorbed gas distribute in pores when considered water is important, because of the huge influence in adsorbed gas prediction.

We divided the reservoir forming process into two parts: early-stage and late stage. In the early-stage of reservoir forming process, shale gas begins to generate when thermal maturation of kerogen reach approximately 1.0% or higher[8]. They are first absorbed on the surface of kerogen. Extra gas are dissolved in liquid-water or place in the spaces between water molecules, as shown in Figure 1 (a). They also diffuse and transport onto the surface of inorganic pore system, as shown in Figure 1 (b). During the million years, the whole reservoir tends to be dissolved and adsorbed gas saturated, entering into the late-stage of reservoir forming process. With the generation of large amounts of gas, pressure and temperature in shale reservoir increased. Free gas forms during the late-stage, as shown in Figure 2 (a). Two essential elements that controls forming and migrating of free gas are: 1) the amount of generated gas must be greater than the amount of shale rock adsorbed; 2) must overcome the strong capillary force from micro-pore in shales. As shale gas generating and free gas forming, the pressure continues to increase. Finally, micro-crack and fracture form when the pressure reaches the fracture pressure of shale matrix, as shown in Figure 2 (b).

![Figure 1. Early-stage of reservoir forming process](image)
2.2. Characteristic of shale pores
The types of shale pores are complex. Due to the sedimentary environment and process, shale forms different types of pores ranging various scales. From characteristics of gas and water distribution, pore system in shales can be divided into two categories: solid-gas system and solid-liquid-gas system.

2.2.1. Characteristic in solid-gas system.
Gas pores are known as thermogenic pores, which are the direct evidence to prove gas generation during coalification[9]. Under the influence of temperature and pressure, large amount of nitrogen, carbon dioxide, hydrogen, methane, etc., and even water produced from organic matter[10]. Water produced in gas pores is so rare that it form as water molecules (gas) instead of bound water (liquid). Since the main product during the gas pore forming process is methane and combined its genesis, gas pores which exits in organic matters belong to solid-gas system.

With the increasing degree of maturity, more micro-pores form in organic matter, provide more superficial area, and adsorb large amount of gas molecules. Gas pores can be divided into residual gas pores and metamorphic gas pores[11,12]. Residual gas pores are formed during the early stage of coalification. Most of them exist as an isolated and has poor connectivity, as shown in Figure 3a. The shapes of them are usually short-linear and even closed because of the high lithostatic pressure of the overlying strata. In later stage, metamorphic gas pores formed. In this stage, large amount of gas produced lead to increasing micro-pores, expanding the pore size and even making the pores communicated or deformation. The shapes of them are usually oval, round tube-like and other shapes and rarely regular circle, as shown in Figure 3b.
2.2.2. Characteristic in solid-liquid-gas system.
Plant tissue pores in organic and mineral pores belong to solid-liquid-gas system. Studies have indicated that a certain water film remains in liquid phase on the surface of mineral pores as its systems are water wetting under the formation conditions[2-4]. As for plant tissue pores, they are the spaces in the residual cell structures of precursor plants, which mainly develop in telinite and fusinite[9]. Studies have also shown that the degradation and gas production process of plant debris is under the environment of water, oxygen and the bacteria / fungi it supplied, shale gas and water produced in the process[13]. Although pore size reduced, water in plant tissue pores consumed, produced and discharged during the deposition and gas production process, but water still retained and occupied in these pores.

The shape of plant tissue pores and mineral are controlled by the shape of the body cavity, mineral shape, genesis and compaction degree during the process of sedimentation. Plant tissue pores in telinite are usually squashed, short-linear and irregularly arranged and star-like or arcuated in fusinite [11], as shown in Figure 4. As for mineral pores, it usually divided into interparticle pores and intraparticle pores. In interparticle pores, many of them triangular and some elongated to rounded to angular. The shape of intraparticle pores is commonly controlled by its origin. Pores are sheet-like in clay particles and micas and take the shape of the precursor in grain and crystal dissolution moldic pores [12], as shown in Figure 5.

Overall, pore system in shales can divide into 2 categories: solid-gas system and liquid-gas system. Gas pores belong to solid-gas system, plant tissue pores and mineral pores belongs to solid-liquid-gas
system. Water forms as water molecules (gas) and continuous phase (liquid) in solid-liquid-gas system. Characteristics of pore system are shown in Table 1.

| Types                           | Size       | Shape                                                                 |
|---------------------------------|------------|----------------------------------------------------------------------|
| Metamorphic gas pores           | 2~750 nm   | short-linear, deformed and even closed                                 |
| Residual gas pores              |            | irregular, bubblelike, round tube-like, elliptical cross sections     |
| Pores in telinite               | 10~145 µm  | squashed, short-linear and irregularly arranged starlike or arcuated, causing the irregular shape of the cells |
| Pores in fusinite               |            |                                                                      |
| Pores between grains            | 30nm~2 µm  | Many are triangular; Some elongated to rounded to angular.            |
| Pores between crystals          |            |                                                                      |
| Pores between clay platelets    |            |                                                                      |
| Pores at the edge of rigid grains |          |                                                                      |
| Intercrystalline pores          |            | Commonly controlled by its origin.                                    |
| within pyrite framboids         |            | In clay particles and micas, pores are sheetlike;                     |
| Intraplatelet pores             |            |                                                                      |
| within clay aggregates          |            | In grain and crystal dissolution moldic pores, the pores can take the shape of the precursor. |
| Pores within peloids or pellets | 10nm~1 µm  |                                                                      |
| Dissolution-rim pores           |            |                                                                      |
| Moldic pores after a crystal    |            |                                                                      |
| Moldic pores after a fossil     |            |                                                                      |

3. Conclusions
Reservoir forming process is divided into two stages: early-stage and late stage. In the early-stage of reservoir forming process, shale gas was first absorbed on the surface of kerogen. Extra gas was dissolved in liquid-water or place in the spaces between water molecules. They also diffused and transported onto the surface of inorganic pore system. In the early-stage, free gas forms during the late-stage, and micro-crack and fracture formed when the pressure reached the fracture pressure of shale matrix.

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References
[1] Chen zhenlin, Wang hua, He faqi, et al. (2011) The Forming Mechanism, Occurrence State and Evaluation Method of Shale Gas. China University of Geosciences Press. The Beijing, China.
[2] Ross D J K, Bustin R M. (2007) Shale gas potential of the lower jurassic gordondale member, northeastern British Columbia, Canada. Bulletin of Canadian Petroleum Geology, 55(1): 51-75.
[3] Ruppert, L. F., Sakurovs, R., Blach, T. P., He, L., Melnichenko, Y. B., & Mildner, D. F. R., et al. (2013). A usans/sans study of the accessibility of pores in the barnett shale to methane and water. Energy & Fuels, 27(jan.-feb.), 772-779..
[4] Yinan Hu, Deepak Devegowda, Alberto Striolo, and Faruk Civan. (2013) Microscopic Dynamics of Water and Hydrocarbon in Shale-Kerogen Pores of Potentially Mixed-Wettability. SPE Unconventional Resources Conference-Canada held in Calgary, Alberta, Canada.
[5] Q. R. Passey, K.M. Bohacs, W.L. Esch, et al. (2010) From Oil-Prone Source Rock to Gas-Producing Shale Reservoir-Geologic and Petrophysical Characterization of Unconventional Shale-Gas Reservoirs. CPS/SPE International Oil & Gas Conference and Exhibition in China held in Beijing.,
[6] Robert G. Loucks and Stephen C. Ruppel. (2007)Mississippian Barnett Shale: Lithofacies and depositional setting of a deep-water shale-gas succession in the Fort Worth Basin, Texas. AAPG Bulletin, 91(4):79–601.
[7] Ambrose, R.J. (2011) Micro-Structure of Gas Shales and its Effects on Gas Storage and Production Performance. Ph.D Thesis, University of Oklahoma, Norman, OK.
[8] Jarvie D M, Hill R J, Ruble T E, et al. (2017) Unconventional shale-gas systems: The Mississippian Barnett Shale of north-central Texas as one model for thermogenic shale-gas assessment. AAPG bulletin, 91(4): 475-499.
[9] S.H. Zhang, S.H. Tang, D.Z. Tang, Z.J. Pan, F. Yang. (2010) The characteristics of coal reservoir pores and coal facies in Liulin district, Hedong coal field of China. Int. J. Coal Geol., 81:117–127.
[10] B Durand (2018). Sedimentary organic matter and kerogen. Definition and quantitative importance[J]. Kerogen, Insoluble Organic Matter from Sedimentary Rocks. Technip, Paris, 13-34.
[11] Shiqi Liu, Shuxun Sang, HuiHu Liu, et al. (2015) Growth characteristics and genetic types of pores and fractures in a high-rank coal reservoir of the southern Qinshui basin. Ore Geology Reviews, 64:140–151.
[12] Tianyi Z , Xiangfang L , Zhengfu N , et al. (2018) Pore structure and adsorption behavior of shale gas reservoir with influence of maturity: a case study of Lower Silurian Longmaxi formation in China[J]. Arabian Journal of Geosciences, 11(13):353.
[13] C. W. Langenberg; Alberta Geological Survey. (1990) Coal Geology and its Application to Coal-Bed Methane Reservoir. Alberta Research Council. The Calgary, Alberta.