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Key factors controlling the gas adsorption capacity of shale: A study based on parallel experiments

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ABSTRACT

This article performed a series of parallel experiments with numerical modeling to reveal key factors affecting the gas adsorption capacity of shale, including shale quality, gas composition and geological conditions. Adsorption experiments for shales with similar OM types and maturities indicate that the OM is the core carrier for natural gas in shale, while the clay mineral has limited effect. The N_2 and CO_2 adsorption results indicate pores less than 3 nm in diameter are the major contributors to the specific surface area for shale, accounting for 80% of the total. In addition, micropores less than 2 nm in diameter are generated in large numbers during the thermal evolution of organic matter, which substantially increases the specific surface area and adsorption capacity. Competitive adsorption experiments prove that shale absorbs more CO_2 than CH_4, which implies that injection CO_2 could enhance the CH_4 recovery, and further research into N_2 adsorption competitiveness is needed. The Langmuir model simulations indicate the shale gas adsorption occurs via monolayers. Geologically applying the adsorption potential model indicates that the adsorption capacity of shale initially increases before decreasing with increasing depth due to the combined temperature and pressure, which differs from the changing storage capacity pattern for free gases that gradually increase with increasing depth at a constant porosity. These two tendencies cause a mutual conversion between absorbed and free gas that favors shale gas preservation. During the thermal evolution of organic matter, hydrophilic NSO functional groups gradually degrade, reduce the shale humidity and increase the gas adsorption capacity. The shale quality, gas composition and geological conditions all affect the adsorption capacity. Of these factors, the clay minerals and humidity are less important and easily overshadowed by the other factors, such as organic matter abundance.

1. Introduction

Higher energy demands and the increasing difficulty for obtaining conventional oil and gas has made unconventional oil and gas, including that from shale, coal seams, tight sandstones, etc., more attractive than ever before in the industry. Shale gas has proven to be the most promising unconventional oil and gas by the shale gas boom in the US over the past few years. Shale gas exists both as free gas within intergranular pores or natural fractures and as absorbed gas on or underneath the surface of insoluble organic matter (kerogen) or inorganic minerals (Ross and Bustin, 2009). Significant amounts of shale gas are produced from the unceasing desorption of the latter, especially during the post-plateau production phase (Li et al., 2007; Xu et al., 2011). Previous studies on what percent of the total produced shale gas was absorbed indicate that it varies in different shales but is usually high, ranging from 40% to 85% (Lu et al., 1995; Curtis, 2002; Li et al., 2007). Lu et al. (1995) observed that most samples contain more absorbed gas than free gas with percentages between 55% and 80%. Li et al. (2007) and Xu et al. (2011) both agreed that absorbed gas caused the good gas preservation in shale. Based on the above findings, an adsorption phase is believed to play an important role in the successful development of shale gas (Curtis, 2002; Montgomery et al., 2005; Jarvie et al., 2007; Li et al., 2007; Nie et al., 2009). Therefore, determining the key factors controlling the shale gas absorption capacity is important. Previously, the evidence almost comprehensively indicated two or more key factors. For example, the relationship between the gas adsorption capacity and TOC may indicate effects

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from OM maturity, temperature, humidity, and so on. It is undeniably more convictive to individually determine these factors. In this paper, we designed and performed a series of parallel absorption experiments.

2. Samples and experiments

The gas adsorption capacity for shale is mainly controlled by geological conditions and the properties of both the adsorbing material (shale) and adsorbates (natural gas). Combining experience gained from the exploration and development practices for shale gas in North America with approaches to studying the coal-bed methane adsorption capacity, we selected Paleogene lacustrine black shale samples from Eastern China for parallel adsorption experiments involving a series of potential key factors (organic matter abundance and maturity, clay mineral, gas composition, temperature, pressure and humidity) that affect the shale gas adsorption capacity. The samples were taken from two important shale oil and gas wells, Anshen1 Well in Biyang the Depression and Shen352 Well in the Damintun Depression. Qualitative analyses and quantitative simulations were performed based on the experimental results. We used artificial aging processes under anhydrous and non-pressurized conditions to prepare samples with different maturities. First, we heated the sample from room temperature to 200 °C and held for 72 h. We then heated the sample another 50 °C at 5 °C/min and held for another 72 h. By repeating this process, we successively prepared samples with a final temperature of 300 °C, 400 °C and 500 °C.

Isotherm adsorption experiments were then performed using the prepared samples with a self-developed high-pressure gas adsorption–desorption instrument mounted on a constant-temperature oil bath with a temperature error limited to ±0.2 °C and pressure accuracy of 3.51 kPa. We used the experimental standards recommended by the American Society for Testing and Materials (ASTM) for these experiments, i.e., to perform the experiments with a reservoir temperature and equilibrium water content (except for the humidity comparative experiments), to simulate real reservoir conditions in the lab. The procedure was as follows: ① weigh the samples (approximately 100 g) with a 0.2 mg accuracy; ② put pre-wetted samples into an incubator with a super-saturated K_2SO_4 solution, which maintains a relative humidity of 96–97% in the incubator; ③ weigh the samples at certain time intervals until a constant weight is obtained (<24 h). The equilibrium water content equals the sum of the approximated water content for an air dried sample and the water content absorbed at equilibrium. The sample humidities can be controlled via the equilibrium water time in the incubator. For the parallel humidity experiments, the times were 0 h (primary sample), 3 h, 6 h and 24 h. Apart from the isothermal adsorption experiments, we also experimentally analyzed the organic carbon, pyrolysis, vitrinite reflectance, rock mineral composition, and both nitrogen and carbon dioxide absorption. Tables 1 and 2 list the sample characteristics and experimental projects.

3. Results and discussion

3.1. Effect of organic matter and clay mineral abundances

Matrix pores in the shale reservoir include residual primary pores, micro-cracks/pores from clay mineral illitization and dissolution pores from instable minerals (e.g., feldspar and calcite) (Jiang et al., 2010). Organic nanopores were identified in kerogen via a combination of argon ion polishing and SEM and may also be important reservoir spaces in shale (Loucks and Reed, 2009). Geologists and geochemists believe the organic matter abundance

Table 1
Basic geochemistry properties for the experimental samples.

Samples	TOC (%)	S_1 (mg/g)	S_2 (mg/g)	Tmax (°C)	Ro (%)	Percent contents of clay mineral (%)						Mineral percent contents (%)									
						K	C	I	S	I/S	%S	Clay mineral	Quartz	Potash feldspar	Plagioclase	Calcite	Dolomite	Ankerite	Pyrite	Hematite	Analcime
Anshen1 (2418.70 m)	1.73	1.13	10.15	444	–	0	4	56	0	40	15	36	12	3	10	0	35	0	4	0	0
Anshen1 (2420.05 m)	0.22	1.11	1.23	445	–	0	2	57	0	41	20	26	8	2	8	6	34	0	4	0	12
Anshen1 (2423.25 m)	0.15	0.95	0.94	443	–	0	2	80	0	18	15	10	36	8	22	2	20	0	0	0	2
Anshen1 (2566.40 m)	0.77	0.74	4.01	447	0.65	0	0	100	0	0	–	10	1	7	49	1	28	0	4	0	0
Anshen1 (2568.35 m)	0.59	1.01	2.63	446	0.66	0	0	100	0	0	–	14	1	4	34	0	27	0	11	0	9
Anshen1 (2570.61 m)	0.47	1.06	2.19	445	–	0	0	100	0	0	–	17	1	5	36	0	28	0	2	0	11
Primary Shen352 sample	5.23	0.67	8.47	443	0.84	5	6	17	0	72	20	54	22	0	7	6	0	8	0	3	0
Matured to 300 °C Shen352 sample	3.14	0.11	0.71	447	0.85	4	5	21	0	70	21	52	24	0	6	5	0	9	0	4	0
Matured to 400 °C Shen352 sample	2.62	0.11	0.66	452	1.21	4	5	18	0	73	21	54	21	0	10	3	0	10	0	2	0
Matured to 500 °C Shen352 sample	2.26	0.12	0.52	461	2.15	6	6	17	0	71	22	55	23	0	6	6	0	6	0	4	0