

Research progress and prospects of CO₂ enhanced shale gas recovery and geologic sequestration

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Abstract. CO₂ injection to strengthen shale gas development is a new technology to improve shale gas recovery and realize geologic sequestration. Many scholars have studied these aspects of this technology: mechanism of CO₂ displacement CH₄, CO₂ and CH₄ adsorption capacity, affecting factors of shale adsorption CO₂, CO₂ displacement numerical simulation, and supercritical CO₂ flooding CH₄ advantages. Research shows that CO₂ can exchange CH₄ in shale formations, improve shale gas recovery, on the other hand shale formations is suitable for CO₂ sequestration because shale gas reservoir is compact. The supercritical CO₂ has advantages such as large fluid diffusion coefficient, CO₂ dissolution in water to form carbonic acid that can effectively improve the formation pore permeability etc., so the displacement efficiency of supercritical CO₂ is high. But at present the technology study mainly focus on laboratory and numerical simulation, there is still a big gap to industrial application, need to study combined effect of influence factors, suitable CO₂ injection parameter in different shale gas reservoir, CO₂ injection risk and solutions etc.

1 Introduction

CO₂ capture and geologic sequestration is a kind of technology of CO₂ emission reduction, many countries have taken it seriously. Shale gas reservoir has the characteristics of low porosity, low penetration and extreme compactness, which results in very low gas recovery ratio of shale reservoirs. Conventional natural gas recovery ratio can reach to about 60%, while shale gas reservoirs recovery ratio is only about 4.7% to 10% without hydraulic fracturing [1]. While fracturing fluid is likely to cause pollution, need to study a new environmental friendly technology for shale gas development. CO₂ injection not only can enhance recovery ratio of shale gas reservoirs, but also can realize the permanent geologic sequestration of CO₂. It is a kind of new technology of CO₂ storage and use. Its application has great significance for shale gas development and environment protection.

2 CO₂ displacement CH₄ mechanism in shale gas reservoirs [2-4]

From the micro, because CO₂ molecular structure is linear, diameter less than the diameter of CH₄, CO₂ can access smaller micro-pore, which increase contact area and contact time of CO₂ with shale reservoirs, sequentially increase CH₄ displacement amount of CO₂ in shale gas reservoirs.

From the adsorption ability, the contrast laboratory experiments of shale adsorption performance of CO₂ and

CH₄ showed that adsorption capacity, adsorption rate and adsorption equilibrium time of CO₂ is better than those parameters of CH₄ in the same experiments time. Numerical simulation model also showed a same result: CO₂ is easier to be adsorbed by shale than CH₄ for CO₂ has stronger adsorption ability.

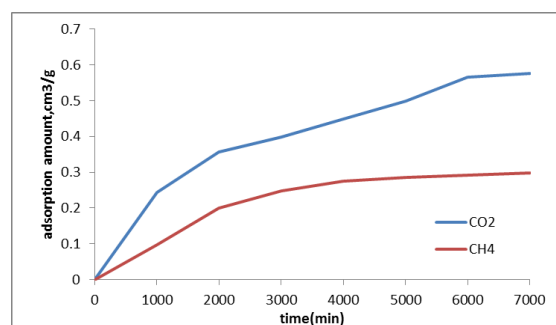


Fig. 1 Isothermal adsorption curves of CO₂ and CH₄ at 35°C with same sample

From the macro, CO₂ replacing CH₄ in shale reservoirs conform to the extension form of the Langmuir equation (equation 1). The injected CO₂ increased the total gas pressure and reduce the CH₄ partial pressure within the shale reservoirs, which will lead to CH₄ desorption from shale to achieve the new adsorption equilibrium.

$$V_i = V_{mi} \frac{\frac{P_{yi}}{P_{Li}}}{1 + P \sum_{j=1}^{nc} \frac{P_{yj}}{P_{Lj}}} \quad (1)$$

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V_i : adsorption amount of gas component i, cm³/g
 V_{mi} : Langmuir adsorption constant of component i, cm³/g
 P : gas pressure in reservoir, MPa
 y_i : Mole fraction of gas component i
 P_{Lj} : pressure of gas component j when adsorption amount of the gas component j reaches to 50 % of the adsorption limitation ,MPa
 nc : numbers of different gas component

3 Influencing factors of CO₂ adsorption in shale gas reservoirs [2-6]

Shale desorption analytical test with shale sample which was made to pieces in a certain size proved that the adsorption of CO₂ in shale is the physical adsorption, which is influenced by temperature, pressure and the mineral composition of shale, moisture content, shale gas composition and other factors:

- 1) Adsorption capacity decrease with temperature increasing;
- 2) Adsorption capacity increase with pressure increasing;
- 3) Temperature and pressure have a comprehensive effect on the adsorption and desorption of shale. Under the low temperature and pressure range, the influence of pressure on adsorption performance is greater than that of temperature. The influence of temperature on adsorption performance is greater than that of pressure in high temperature and pressure condition;
- 4) Adsorption capacity increase with the content of organic matter increase. Montmorillonite with more calcareous has the highest CO₂ adsorption capacity, while CO₂ adsorption capacity of kaolinite is the least;
- 5) Pore structure has an influence on the adsorption capacity;
- 6) When there are water in the shale gas reservoir, CO₂ will dissolve in water to form carbonic acid to erode the formation and increase CO₂ adsorption, which can effectively improve the permeability of the formation and increase shale gas production;
- 7) CO₂ will produce convection diffusion with shale gas with CO₂ injecting which will form a CO₂ - shale gas multivariate system. The shale gas content is bigger, the easier retrograde condensation occur, it will influence CO₂ adsorption and the way of shale gas production.

Above conclusion is almost same at shale desorption analytical test with shale samples which was preserved the original core structure, compared with the test that simulated shale reservoir environment.

4 CO₂ displacement laboratory test with shale core sample [2,7]

Studies showed that temperature and pressure of CO₂ injection have important effect on shale gas recovery. The recovery ratio increase with CO₂ injection temperature and pressure increasing.

Table1. CO₂ adsorption experiment data of shale sample1

35°C		45°C	
Balance pressure,M pa	Adsorption amount,cm ³ /g	Balance pressure,Mp a	Adsorption amount,cm ³ /g
2.06	0.921	2.82	0.032
3.78	0.356	4.41	0.11
6.02	0.806	7.06	0.201
8.02	0.998	8.46	0.365

Table 2. CO₂ adsorption experiment data of shale sample2

35°C		45°C	
Balance pressure,M pa	Adsorption amount,cm ³ /g	Balance pressure,Mp a	Adsorption amount,cm ³ /g
1.93	0.038	2.38	0.035
3.62	0.11	3.12	0.098
5.08	0.198	4.41	0.143
6.16	0.239	5.08	0.221

Gas recovery ratio is different at different producing start time under the condition of CO₂ injection. Injecting CO₂ 10 hours later, the competitive adsorption of CO₂ and CH₄ is sufficient. The gas recovery ratio is higher than that gas production start at the same time of CO₂ injecting. The reason is that the concentration of CO₂ in the shale reservoirs or the CO₂ partial pressure is low when CO₂ inject for a short time, the displacement amount of CH₄ is very low. After enough competition adsorption, CO₂ will spread deep into the shale matrix and displace CH₄ more. At the same time, the shale volume will expand after a large amount of CO₂ adsorption, so that the pore adsorbed CH₄ will open again and CO₂ will displace the inner CH₄ of shale, which will increase the recovery ratio.

5 Numerical simulation of CO₂ displacement shale gas [3,6]

The numerical simulation simulated the influence on recovery ratio of CO₂ injection timing, CO₂ injection rate, and the influence of crack numbers. The results showed that CO₂ injection parameters exists an optimal value. Multi-stage horizontal fracture will increase the crack number, but it will not improve gas recovery ratio obviously.

The concept model of CO₂ displacement CH₄ of shale showed that displacement process can be divided into two situations: at low CO₂ injection pressure, shale samples with smaller micro-pore ratio surface area and smaller micro-pore volume ratio have higher CO₂ sequestration ability. While at higher CO₂ injection pressure, shale samples with larger micro-pore ratio surface area and smaller micro-pore volume ratio have higher CO₂ sequestration ability.

6 Supercritical CO₂ exploitation shale gas [8,9]

CO₂ critical temperature is 31.1 °C, critical pressure is 7.38 MPa, critical density is 0.448 g/m³. When the temperature and pressure of the shale gas reservoir are greater than the critical temperature and pressure, the injected CO₂ reaches the supercritical state. Supercritical CO₂ has the excellent characteristics different from the conventional liquid, gas, which can improve reservoirs pore and fissure development level, can improve the reservoirs permeability significantly, etc. Supercritical CO₂ can improve the single well production and gas recovery ratio of shale gas reservoirs with these characteristics.

First, supercritical CO₂ viscosity is low, diffusion coefficient is larger than that of CH₄, and the most important is its surface tension is zero. Therefore, it is very easy to flow into the reservoirs pore, and able to enter into any space greater than CO₂ molecular. Under the effect of external force, the supercritical CO₂ can displace free CH₄ in the tiny pore and fracture effectively. Second, supercritical CO₂ fluid density has strong ability of solvating, it can dissolve pollutants near wellbore area, reduce the flow resistance, increase shale reservoir permeability, which is benefit to shale gas production. When temperature and pressure of environmental conditions is higher than CO₂ critical condition, the density of CO₂ is more close to the density of the fluid, then the property differences between supercritical CO₂ and shale gas increases, which lead to the convection diffusion effect abating. Supercritical CO₂ displacing shale gas likes a piston displacement process under high pressure and temperature. That will increase displacement efficiency. In addition, the viscosity of supercritical CO₂ is much higher than that of shale gas. In higher pressure, the displacement efficiency improves with the increasing of the viscosity difference.

7 Technical prospect and further research Suggestions

The technology compared with the traditional fracturing technology, has these advantages: water saving, environmental protection, simple process, has a broad development prospects, but at present the main research forces on laboratory test and numerical simulation. In order to realize its industrialized application as soon as possible, still need to strengthen following research:

1) The adsorption and desorption performance of shale gas are influenced by many factors. At present, most researches are studies on a certain factor independently. The effects of multiple factors are not studied or less. In the future, it is necessary to study the results of the combined effects of various factors under stratigraphic conditions.

2) Needs to study CO₂ injection pressure, CO₂ injection temperature and CO₂ injection timing of different characteristics shale gas reservoirs, to determine the reasonable CO₂ displacement parameters.

3) Select 1 or 2 integrity shale gas reservoirs to carry out pilot test, verify the laboratory test and numerical simulation research, form series technology which adapt to shale gas reservoirs development with different depth, temperature, pressure ;

4) Needs to study whether is shale gas reservoirs still suitable for CO₂ geologic sequestration or not after the implementation of the fracturing measures;

5) Due to the corrosive effects of CO₂ and the risk of CO₂ leakage, it is necessary to strengthen the study of risk identification and risk countermeasures.

References

Here are some examples:

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