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The effects of mineral components and pore structures on CH_4 breakthrough pressure.

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Outline

1. Introduction
2. Samples and experimental apparatus
3. Experimental methods
4. Results and discussion
5. Conclusion

Introduction

Shale Gas Revolution

Global shale gas resources are abundant and could be as high as 208 trillion cubic meters according to the IEA. In recent years, shale gas resources have attracted attention in many countries. Shale gas is abundant and it is regarded as an important additional, but unconventional, energy source. With the emergence of horizontal well and hydraulic fracturing technology, shale gas production has been promoted significantly on a global scale.

Shale gas accounts for a considerable proportion of the recoverable unconventional gas resources in all the countries.

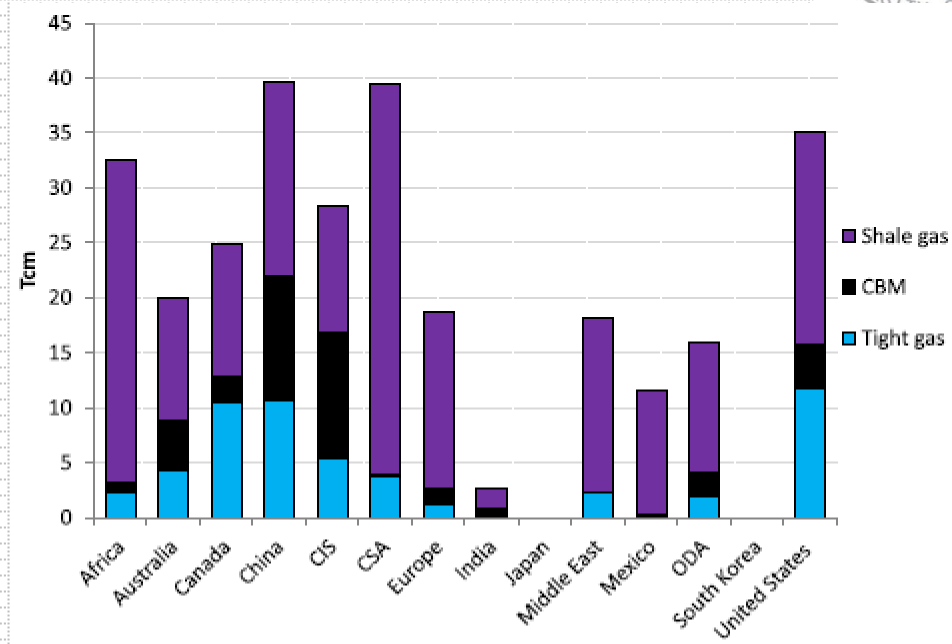


Fig.1 Regional distribution of the recoverable unconventional gas resources(CBM, coal bed methane; Tcm, trillion cubic meters) (McGlade et al., 2013)

Shale Gas in China

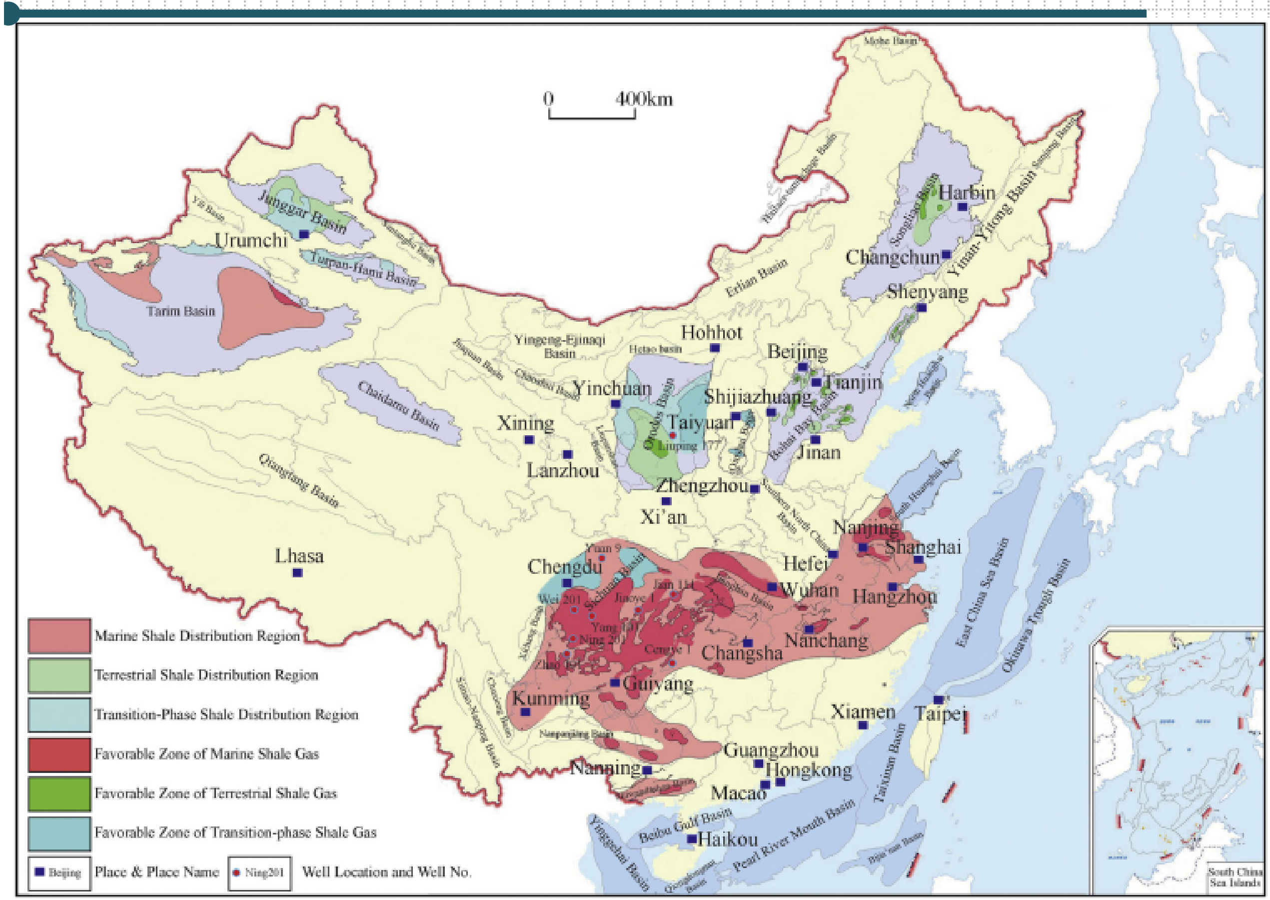


Fig.2 Distribution of Organic-rich shales in China （Jiang et al., 2015）

Breakthrough Pressure in Shale Gas

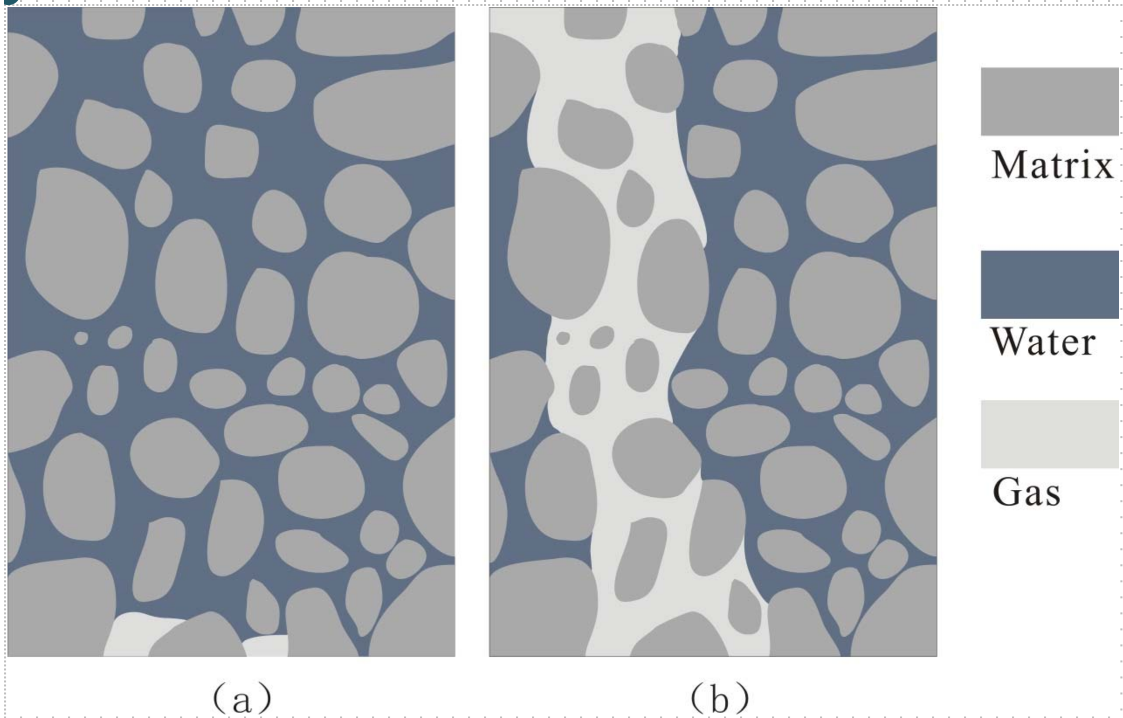


Fig.3 Two key points in process of gas flow in water-saturated rock: (a) Pc=Pc,e, gas started to permeate into the rock, and (b) Pc=Pc,b, gas flow pass the rock and gas leak is observed from the outlet of the rock

Shales underground is a mixture system of gas-water-solid phase and migration mechanism is complex. Breakthrough pressure is not only the key parameter to estimate the sealing efficiency of the shale caprocks but also closely related to shale gas migration.

However, it is difficult to accurately distinguish the capillary entry pressure and the capillary breakthrough pressure by means of experiment and they are considered to be almost equal. (Fig.3)

During our investigation, the pressure at which gas was monitored at the outlet was recorded as the breakthrough pressure.

Breakthrough Pressure in Shale Gas

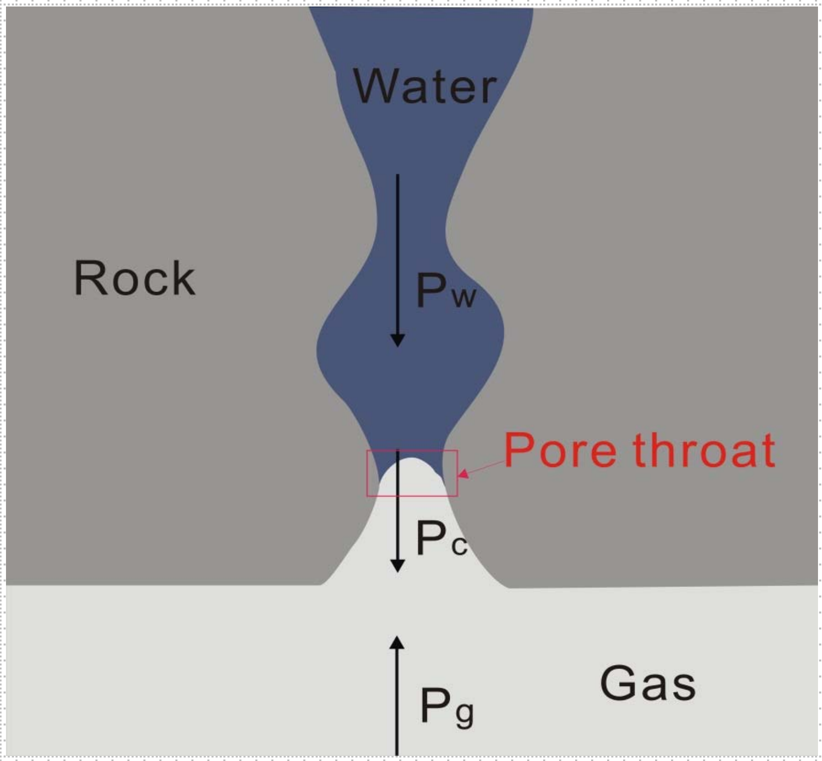


Fig.4 Gas breakthrough mechanism on a pore throat scale.

Fig.4 presents gas breakthrough mechanism in a pore throat. Capillary pressure (Pc) in the low porous media in pore scale can be described by the Lapla
ce equation:

$$P_c = P_g - P_w = \frac{2\sigma cos\theta}{r}$$

Where Pg and Pw are pressure of the gas phase and the water phase, respectively, σ is the interfacial tension (IFT), θ is the contact angle, and r is the radius of the largest pore throat in the porous media.

Samples and Experimental Apparatus

Samples

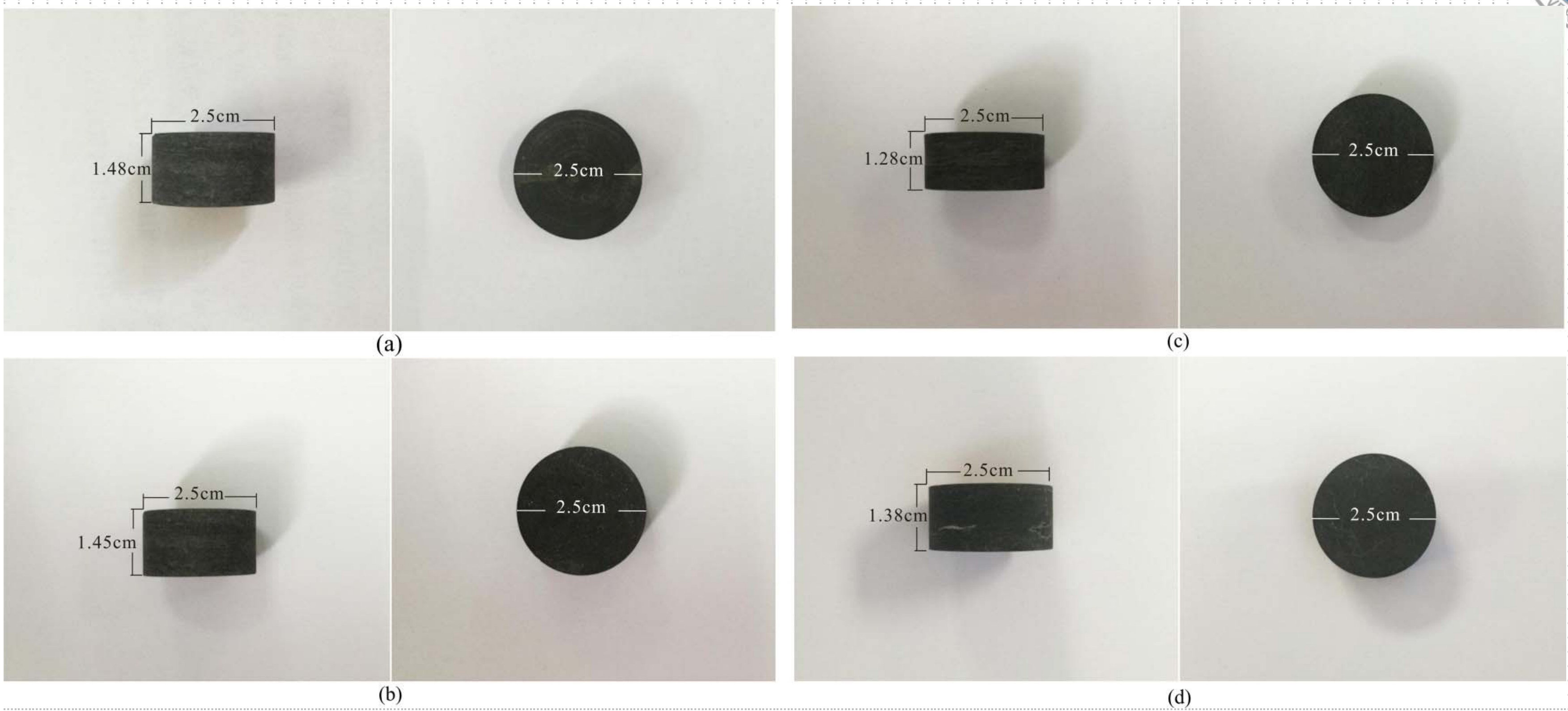


Fig.5 Shale samples

Apparatus

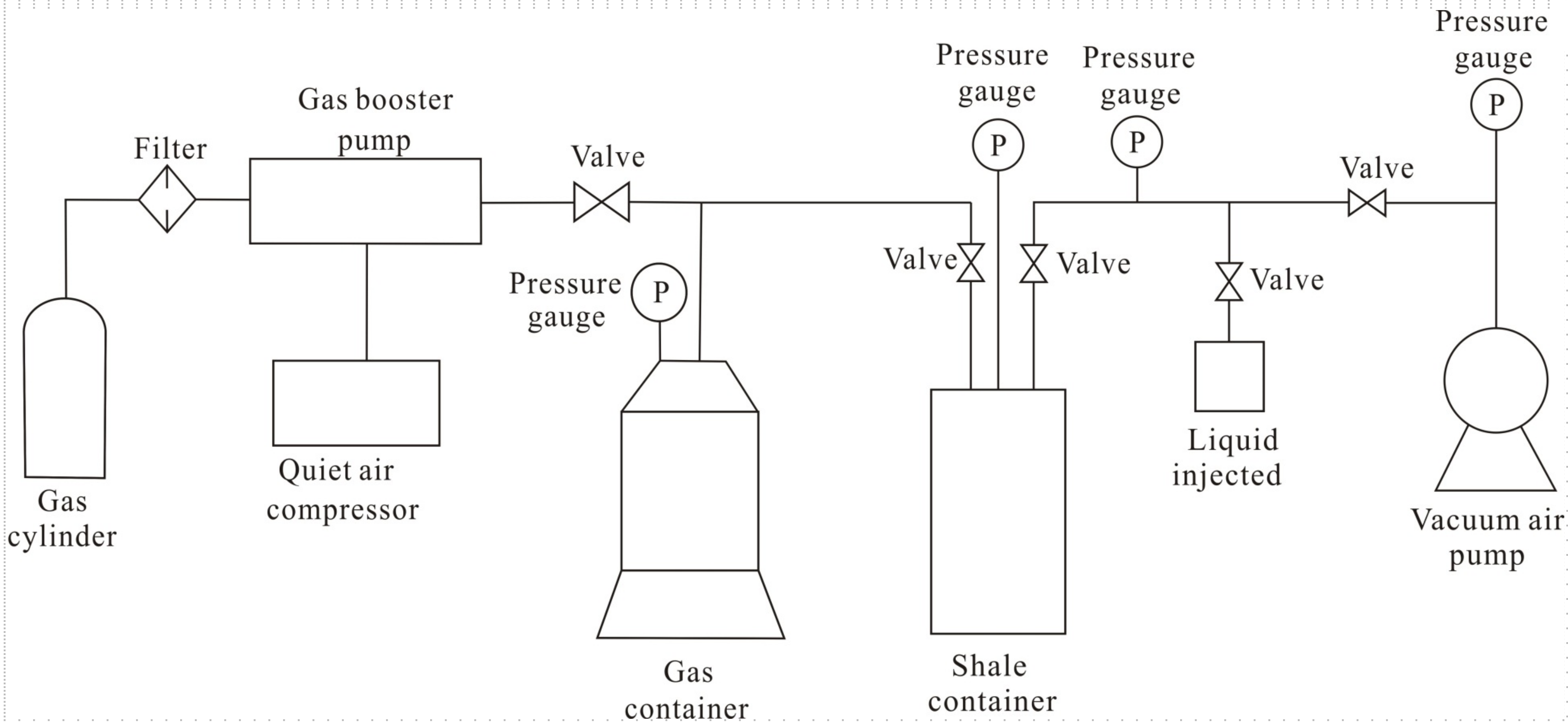


Fig.6 Schematic diagram of the water saturation experimental apparatus.

Apparatus

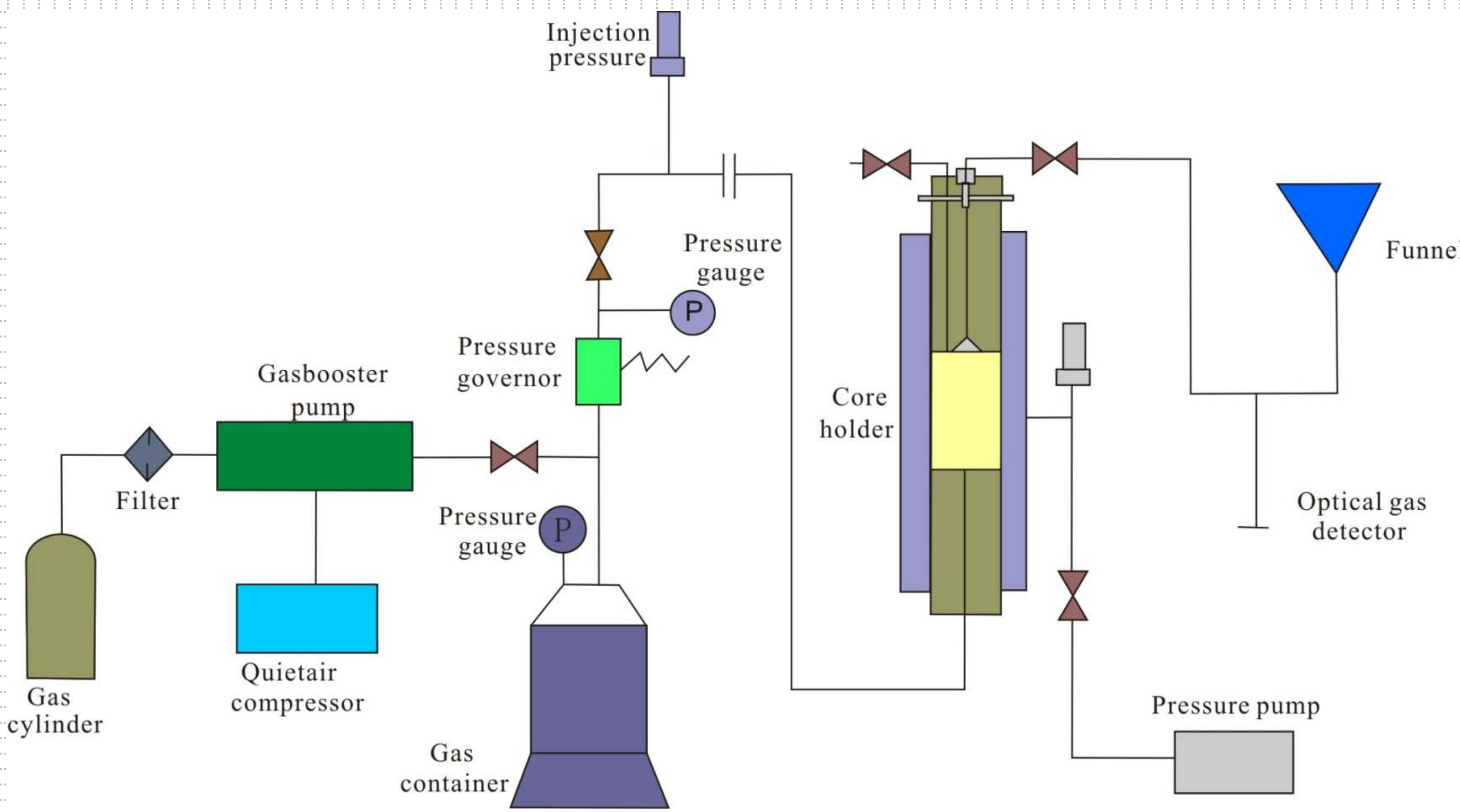


Fig.7 Schematic diagram of the breakthrough pressure detection apparatus.

M Experimental Methods

Geochemical analyses

Quantitative X-ray results show that the Carboniferous shale cores from the Chaiye2 borehole are quartz-dominated (> 40%) with low amounts of microcline and siderite among the non-clay minerals. Illite-smectite accounts for the majority of the clay mineral content in the four shale samples.

Mineralogical composition of the samples based on X-ray diffraction (XRD) analysis

Sample number	Quartz (%)	Calcite (%)	Ankerite (%)	Albite (%)	Pyrite (%)	Siderite (%)	Microcline (%)	Clay (%)
C012	57	6	5	5	2	-	-	25
C022	40	3	6	7	4	-	-	40
C039	57	-	7	3	3	-	1	28
C040	49	-	-	7	2	-	-	42

Geochemical analyses

Table1. Clay composition and content for the four shale samples

Sample number	Illite smectite mixed layer (%)	Illite (%)	Kaolinite (%)	Clinochlore (%)
C012	54	18	18	10
C022	54	9	28	9
C039	53	10	29	8
C040	55	8	29	8

Table1. Shale sample properties

Sample number	Depth (m)	TOC (%)	Kerogen type	vitrinite reflectance (Ro)
C012	956.00	0.62	II2	1.56
C022	996.50	1.67	II2	1.49
C039	1047.2	1.64	II2	1.65
C040	1048.2	2.88	II2	1.59

Properties of Carboniferous shale used in present study are approximately in accordance with Sichuan Longmaxi shale and Mississippian Barnett shale (Pan et al., 2015).

Microstructural characteristics

Micstructural characteristics were studied by Field emission scanning electron microscope (FE-SEM).

Pore size distribution of micropores and mesopores were obtained by low tempereture CO_2 and N_2 adsroption experiments, respectively. Analyses of pore size distribution of micropores (diameter<2nm) and mesopores (2<diameter<50nm) were analyzed using the density functional theory (DFT) and Barrette-Joynere-Halenda (BJH) model, respectively in this study. And pore size distribution of macropores (diameter>50nm) were obtained by mercury intrusion method.

Breakthrough experiments

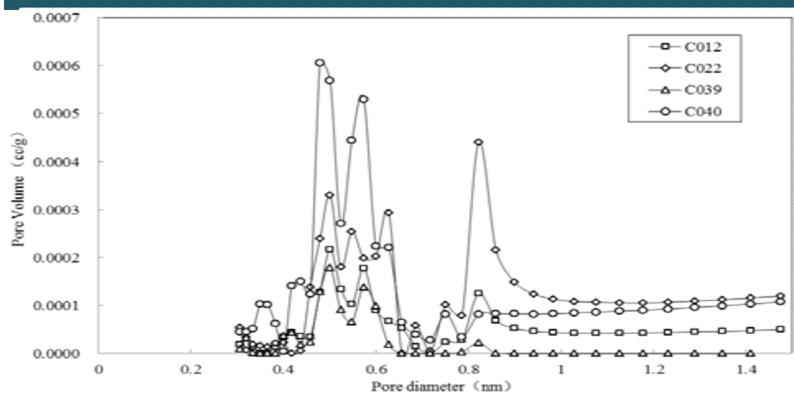
All the breakthrough pressure experiments were conducted strictly according to the Measurement of Gas Breakthrough Pressure in Rock (Standards of the People's Republic of China of the Petroleum and Natural Gas Industry, SY/T 5748-1995).
The apparatus was designed to use a SBS approach first proposed by Thomas et al. (1968). Under the experiment condition of SBS approach, the sample state and gas penetration process are almost the same as in reservoir condition underground (Boulin et al., 2013).

Table3. Experimental pressure and

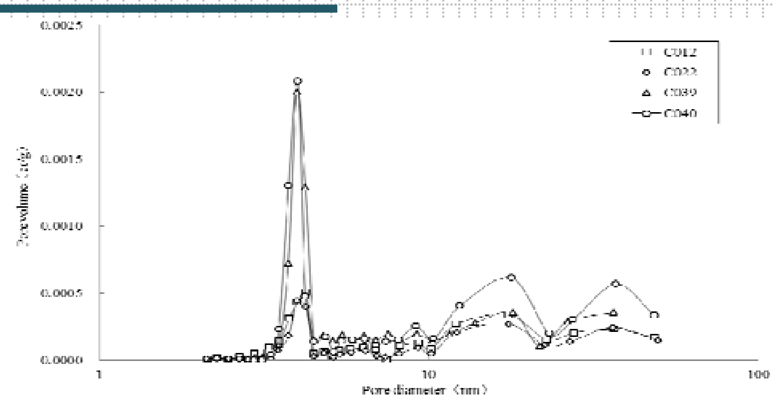
Pressure/MPa	time interval/min	Pressure interval/MPa
P≤2	30	0.2
2<P≤5	45	0.5
5<P≤10	60	1
10<P≤15	90	1
15<P	120	1.5

Results and Discussion

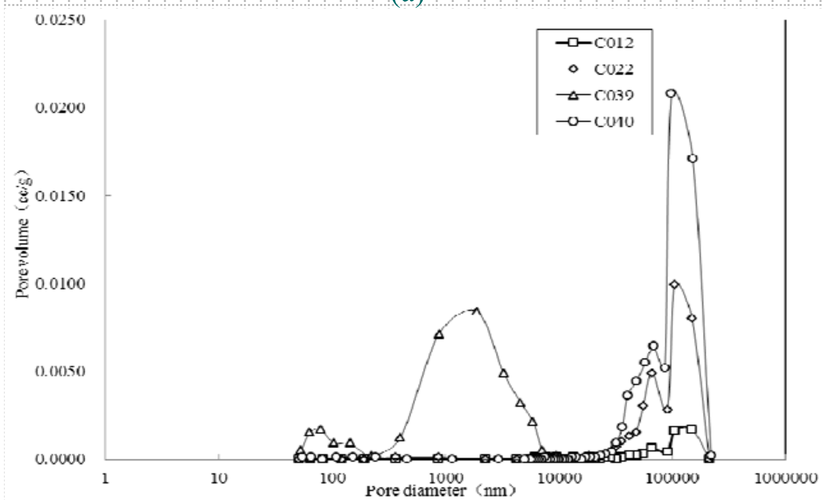
Pore-structure parameters



(a)



(b)



(c)

Fig.8 Pore size distributions of samples C012, C022, C039, C040 (a) low-pressure CO2 adsorption (b) low-pressure N2 adsorption (c) high-pressure mercury intrusion.

Effects of saturation on breakthrough pressure

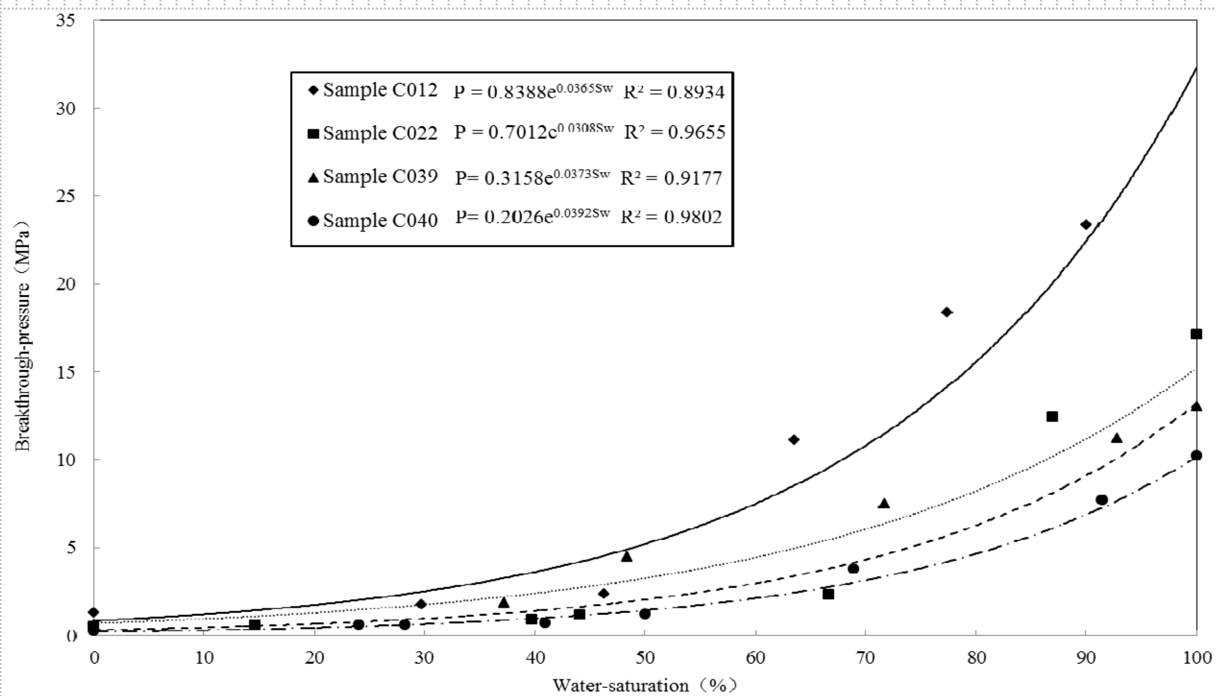


Fig.9 Comparison of the breakthrough pressure curves of the four samples (P: breakthrough pressure; Sw: water saturation).

Breakthrough pressure increases with water saturation can be observed. For all four samples, the increase in breakthrough pressure with water saturation can be described approximately by the following equation:

$$P = Ae^{BSw},$$

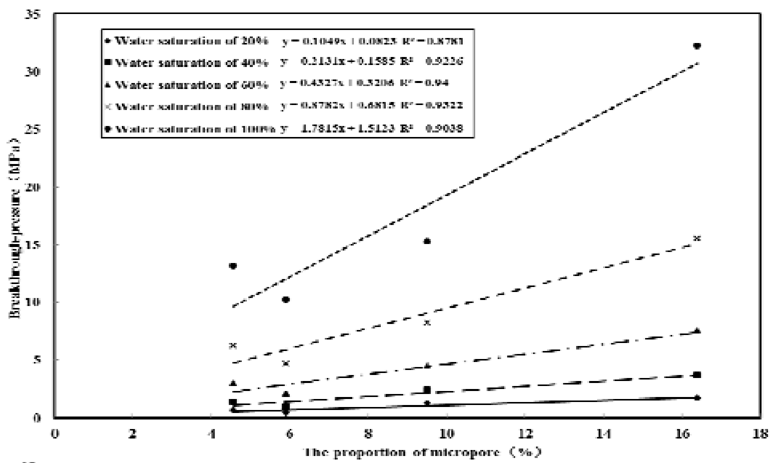
The value of A equals the value of P when Sw is zero, and is the breakthrough pressure of the dry sample.

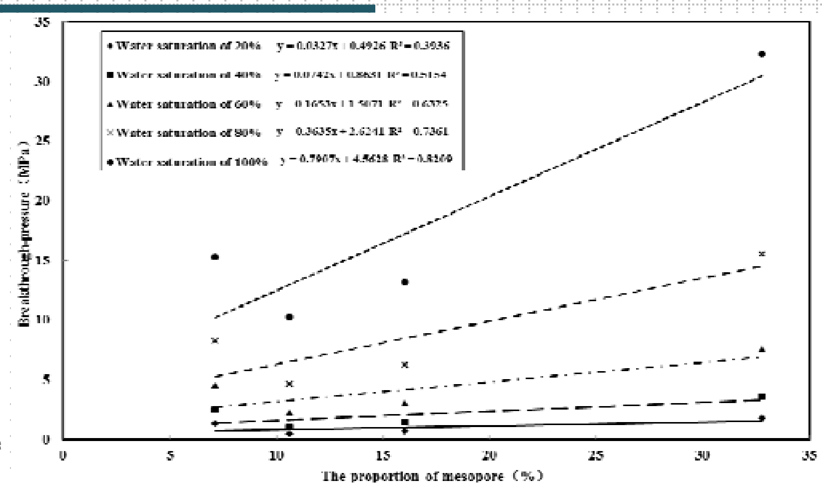
Effects of saturation on breakthrough pressure

With increasing saturation, water films will accumulate on the surfaces of the passages so that some narrow pore throats will be saturated with water. Bound water films attached to the surface of the rock particles have the properties of a solid and cannot be freely removed. A reduction in the effective pore throat radius accompanies the saturating process because of the increasing amount of water in the pores until all the pathways are saturated with water.

Clay minerals are hydrophilic minerals with a small particle size. After being saturated with water, the clay minerals will hold water and swell, and then become barriers to water. The swelling capacity of clay increases with the increase of water saturation. Many pores with narrow diameters will close and the connectivity of gas flow pathways becomes poor because of the swelling of the clay minerals. According to the Laplace equation, the capillary pressure that gas flow must overcome will increase as the effective pore diameter decreases. Therefore, with an increase in water saturation, the swelling of clay minerals also contributes to the increase in the breakthrough pressure.

Effects of pore structure on breakthrough pressure





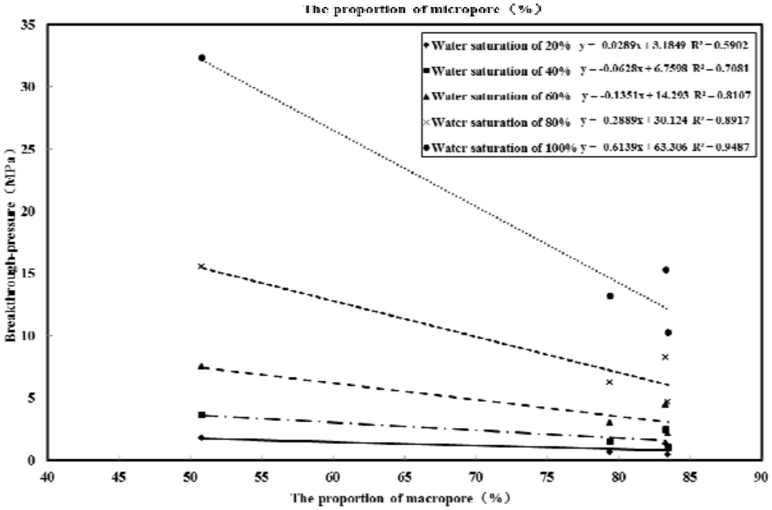


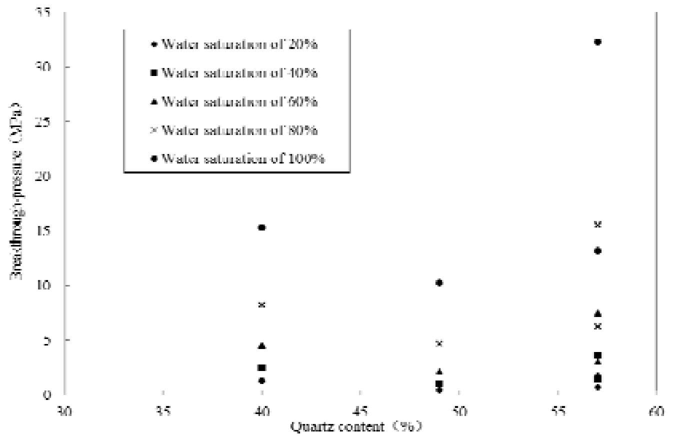
Fig.10 Relationships between proportion of each scale of micropores and breakthrough pressure (P: breakthrough pressure; r: ratio of the micropores).

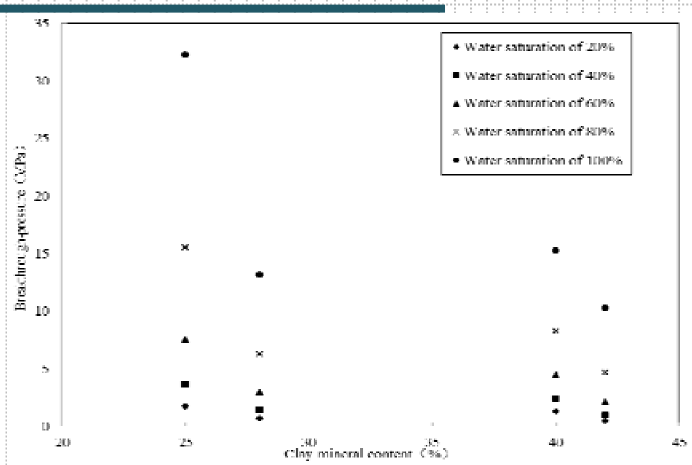
The higher the proportion of micropores, the lower the breakthrough pressure. The situation is the opposite for the proportion of macropores—breakthrough pressure decreases with increased macropore proportions.

Effects of pore structure on breakthrough pressure

Combing the results of our FE-SEM experiments, microfractures present in our samples with lengths of up to dozens of micrometers. These microfractures contribute to the proportion of macropores (diameter > 50 nm) and provide gas pathways. Therefore, gas migration mainly occurs along these large-scale fractures. In each sample, the micropore volume is too small compared with macropore volume so that capillary pressure generated by the micropores is much lower. In addition, the macropores are not as easily sealed off. Thus, shales with a higher proportion of macropores tend to have lower breakthrough pressures.

Effects of dominant mineral composition





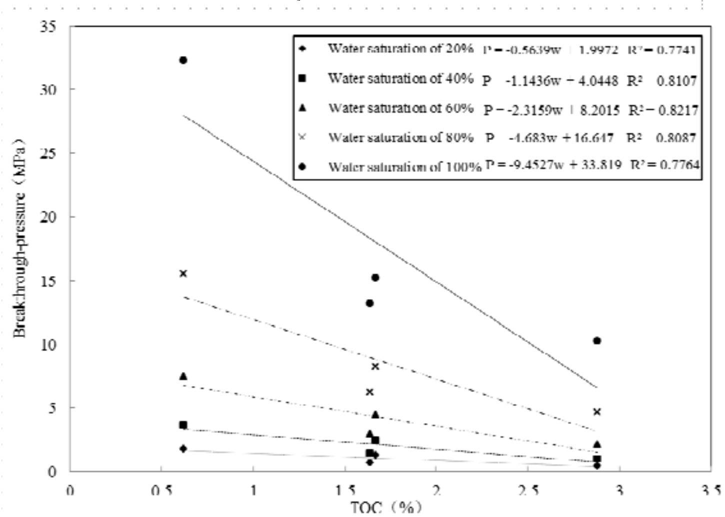


Fig.11 Relation between quartz, clay mineral content and TOC and breakthrough pressure (P: breakthrough pressure; w: content (%)).

Effects of dominant mineral composition

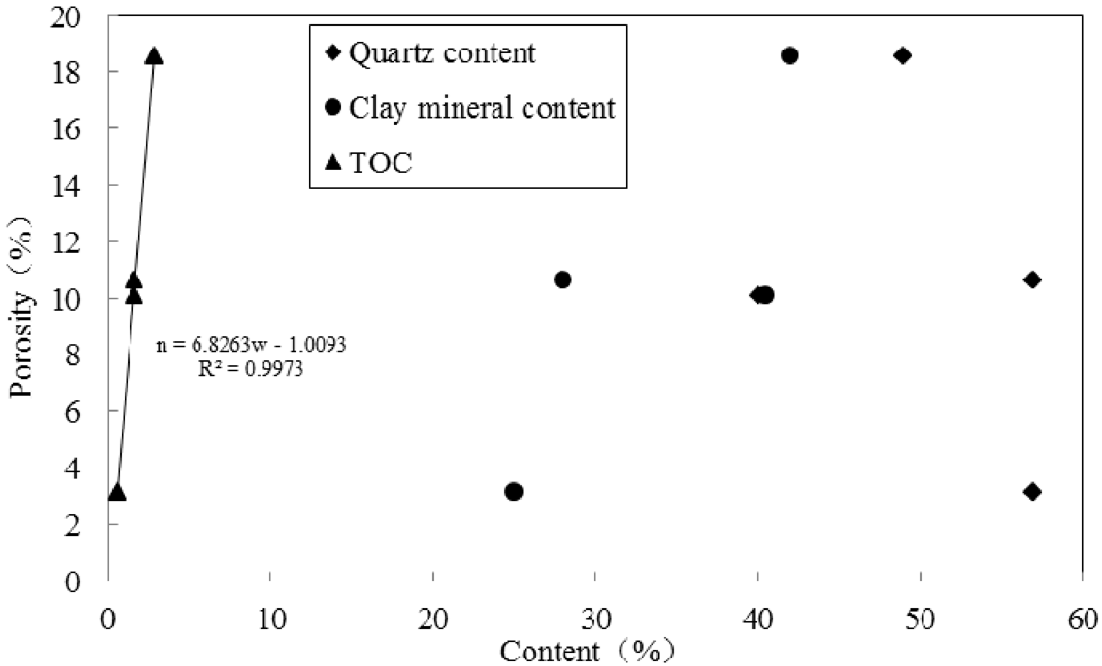


Fig.12 Relationship between quartz, clay and TOC content, and porosity (n: porosity; w: content (%)).

Combing these correlations, the decrease in breakthrough pressure with TOC content can be attributed to variations in porosity.

Conclusion

Conclusions

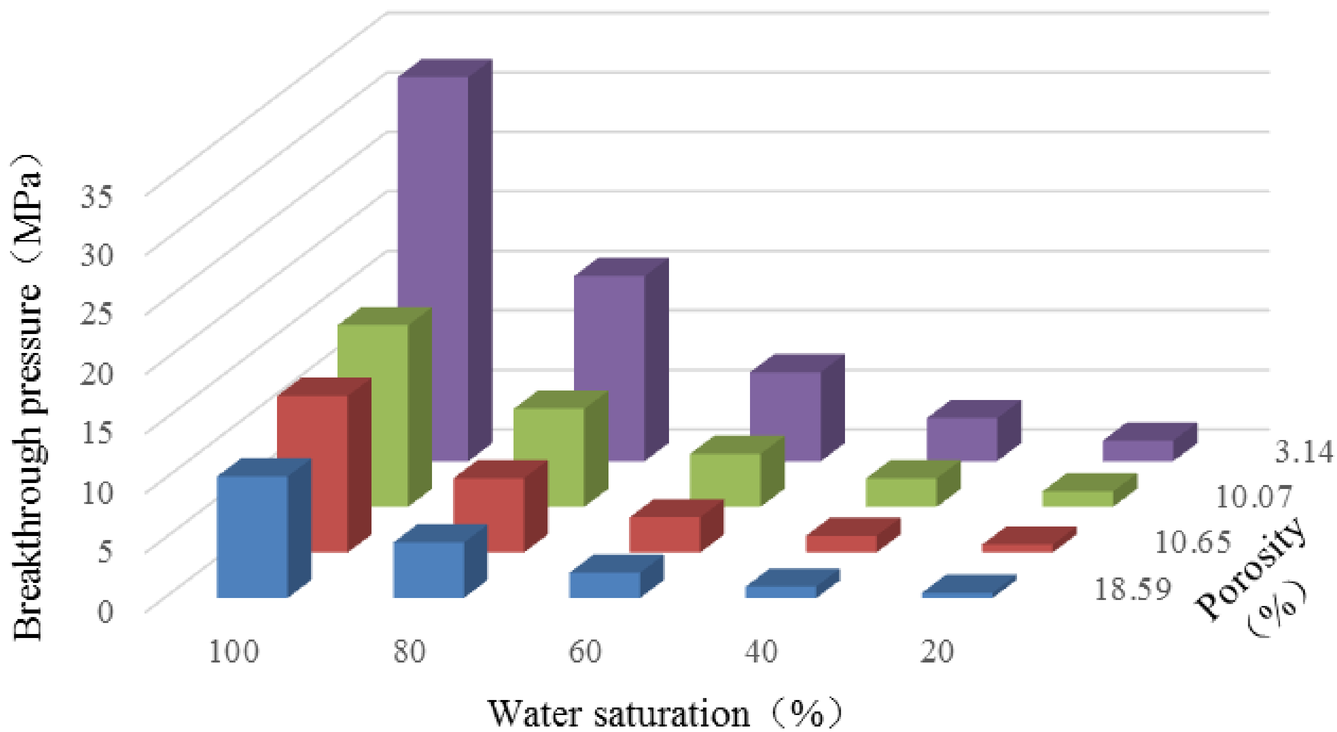


Fig.9 Graph of breakthrough pressure versus porosity versus water saturation for the four samples.

Conclusions

Breakthrough pressure increases exponentially with water saturation according to: $P = Ae^{BSw}$,

The decrease in effective pore diameter caused by both the bound water films and the swelling of the clay minerals resulted in the increase in the breakthrough pressure according to the Laplace equation.

The proportion of micropores is negatively related to the breakthrough pressure, while the proportion of macropores was positively related to breakthrough pressure. In contrast to the micropores, the macropores in our samples consisted of many microfractures with lengths of up to dozens of micrometers, and these macropores not only provided pathways for gas but are also not easily sealed off. As a result, breakthrough pressure decreases with the increase of the proportion of macropores.

Microfractures at the micron level, rather than the quartz dissolution pores and intergranular pores in clay, , made the most significant contributions to the amount of the macropores. Therefore, TOC in these four samples makes the biggest contribution to the proportion of macropores, and thus TOC content shows the great correlation with the breakthrough pressure.

Thank you！