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Permeability evolution of pyrolytically-fractured oil shale under in situ conditions

Fuke Dong[1,2], Zi-jun Feng[1,3,*], Dong Yang[1], Yangsheng Zhao[1,3], Derek Elsworth[4]

1 Key Laboratory of In-situ Property-Improving Mining of Ministry of Education, Taiyuan University of Technology, Taiyuan, Shanxi, China 030024

2 Hebei Vocational College of Geology, Shijiazhuang, Hebei, China 050081

3 Department of Mining Engineering, Taiyuan University of Technology, Taiyuan, Shanxi, China 030024

4 Energy and Mineral Engineering & Geosciences, EMS Energy Institute and G[3] Center, The Pennsylvania State University, University Park, PA 16802, USA

Corresponding author: Zijun Feng, E-mail: fzj3893811@126.com, Tel: 86-351-6014865

Abstract: In-situ injection of steam for heating of the subsurface is an efficient method for the recovery of oil and gas from oil shale where permeability typically evolves with temperature. We reported measurements on Jimusar oil shales(Xinjiang, China) at different temperatures to 600℃ and under recreated in situ triaxial stresses to obtain permeability evolution with temperature and stress. Permeability of tight oil shales evolves with temperature to a threshold temperature and peak temperature. The threshold temperature was subjected to triaxial stresses. For Jimusar oil shale, the threshold temperature ranges from 200℃ to 250℃ at ground stress of buried depth of 500m and from 350℃ to 400℃ at buried depth of 1000m. The peak temperature was almost not subjected to triaxial stress and the range is from 450℃ to 500℃ for all Jimusar samples. Pyrolysis plays an important role in permeability evolution and fundamentally changes permeability tendency and magnitude. At high temperature permeability exhibits a little reduction due to stress effect but still remains a high level due to pyrolysis. The above results show that oil shale mass can change from tight porous media into highly permeable media and oil & gas can easily flow through oil shale stratum.

Keywords: Oil shale; Permeability; Pyrolysis; High temperature and high pressure

1. Introduction

Oil shale is an attractive supplemental energy source for petroleum. China is rich in oil shale

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reserves with 4.76×10^{10} tons that could significantly increase the petroleum supply[1]. It is known that oil shale in-situ mining may be an environmentally friendly method to recover hydrocarbons as excavation, retorting, then spalling is not required. In the in-situ process of mining, heat is injected into the oil shale stratum and causes the organic matter to pyrolyze. Then, the shale oil and hydrocarbon gas can be recovered [2-5]. The advantages of such in-situ mining technology involves no large-scale mining equipment, no waste-rock production and controllable environmental pollution.

Permeability is a key parameter which controls the potential to recover the retorted chemicals from the geological host. Many factors influence rock permeability ,——paramount among them are effective stresses and temperature. At room temperature, the permeability of intact and fractured rocks, generally decreases with increasing effective stresses[6-10]. Rock permeability can be enhanced by thermal fracturing when rock is heated up to high temperature. The permeability of Beishan and Daqing granites which are processed the heating treatment and cooled down to room temperature has been shown to first increase slowly at low temperature, then appears mutation in the range of temperature threshold at temperature transit from 20℃ to 900℃. Beishan granite threshold value of permeability is between 300℃ to 400℃and Daqing granite threshold value of permeability is between 200℃to 300℃[11]. The real-time permeability evolution of Luhui granite with 200 mm in diameter by 400 mm long has been turned out to have a threshold temperature(Tc) of permeability change with temperature in thermally cracked granite. The magnitude of permeability is 10^{-7}D with a low increase below Tc and the permeability whose magnitude is 10^{-6}D increases drastically with high amplitude at 300–400 ℃ while the magnitude is 10^{-5}D at 400 ℃[12]. The permeability of sandstone which was first heated to the set temperature, then cooled down to room temperature has been found out to have the critical temperature of permeability behavior of sandstone identified as 400-500℃. The initial permeability of sandstone under certain pressure conditions was found to increase nonlinearly with the increase in temperature [13]. Zhang performed real-time permeability experiments on fine feldspar sandstone and the results showed that permeability first increases at low temperature, then increases abruptly at the range of threshold temperature of 200℃, and then decreases at the temperatures between 200 and 400℃, and at last increases from 400℃ to 600℃[14].

The above researches mainly focus on permeability evolution with temperature of rocks

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composed of inorganic minerals. Very few of studies on the permeability of organic-matter-rich rocks such as coal and oil shale were performed at different temperature. However, such these studies are mainly related to engineering including coal underground gasification, oil shale and low-rank coal in-situ extraction by injecting heat. Hence, permeability of organic-matter-rich rocks is also significant in these engineering. Permeability sensitivity to reservoir temperature change is crucial for fluid flow as an increase temperature will cause a loss in productivity in oil and gas wells. Permeability of low-rank lignite exhibited total increasing and period change at temperature from room temperature(RT) to 650℃ [15]. Feng studied the permeability of anthracite and gas coal masses under high temperature and triaxial stress and found that coal permeability could be divided into three stages by the critical temperature and peak temperature from room temperature(RT) to 600℃. The critical temperature of anthracite is from 150 ℃ to 200 ℃ and the peak temperature is between 450 ℃ and 500 ℃, the range from 200 ℃ to 250 ℃ is the critical temperature of gas coal and the peak temperature does not emerge from RT to 400℃[16]. In order to study oil & gas flow properties in oil shale stratum during in-situ extracting oil shale by injecting heating, Kang reported his preliminary results on quantity of fissure observed by CT imaging technology in heated Fushun oil shale. It was demonstrated that a small quantity of micro—fissures formed in the specimen mainly along the raw original bedding and the border of hard mineral particles under 300 ℃ and the thermal fissure surfaces were basically parallel to the original bedding. The quantity, length and width of the fissures increased rapidly at above 300 ℃ due to chemical reaction in oil shale [17-18]. The corresponding permeability coefficient was measured at temperature up 500℃ and triaxial stresses and the results showed that permeability dramatically grew at about 350℃. Zhao et.al also studied evolution of pore structure and porosity of Daqing and Yan'an oil shale by CT imaging technology and concluded that thermal decomposition of organic matter at high temperatures was a major factor causing changes in the internal structure of Daqing oil shale. When the temperature exceeded 200℃, large heterogeneous pores were formed in the originally solid material due to the expulsion of the gas and oil generated by thermal pyrolysis of organic matter at high temperature. With a further increase in temperature, the pores expanded and became interconnected by fractures. The heterogeneous thermal expansion was a major factor causing changes in the internal structure of Yan'an oil shale. After the temperature reached 200 °C, numerous fractures parallel to the primary strata were formed, which propagated and expanded with

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increasing temperatures. High temperatures changed the compact structure of oil shale into a porous medium with well-developed pores and fractures[19].

Oil shale permeability is a key parameter in in-situ mining oil shale, which can reflect conducting fluid ability of oil shale stratum, heating transferring between hot medium injected into stratum and oil shale stratum, shale oil recovery, et.al. Xinjiang is rich in oil shale resources and the extracting program are in preparation. Hence, in order to evaluate the economical and technical efficiency of mining before development, experiments about effect of temperature at temperature up to 600℃ on oil shale was carried out for Jimusar oil shale in Xinjiang at triaxial stresses.

2. Experimental method and procedures

2.1 Samples

Big oil shale blocks were collected from an open-pit mine in Jimsar, Xinjiang province in China. They were coated with paraffin wax to maintain natural water-saturated state. All samples were first cored from big blocks and then were lathed into standard size of 50mm in diameter and 100mm long. Length direction of all samples was perpendicular to bedding. Seen in fig.1, the samples are gray and have silty structure with density of 2.40g/cm^3. Proximate analysis and elemental analysis of samples are shown in Table. 1 and 2.

2.2 Experimental procedures

Rock mechanics test system for high temperature and triaxial stresses was employed to perform oil shale permeability measurement at temperature up to 600℃ and triaxial stress. Axial stress to sample was applied by hydraulic piston and confining pressure was transferred to sample by compressed gas. The sample was well sealed by red copper shown in fig.2. Temperature in the sample was measured by thermal couple and heating rate of 15℃/hour was applied and controlled by a set of heating system.

Two in-situ ground stress levels were applied to the samples. For samples 1$^\#$ and 2$^\#$, axial stress of 12.5MPa and confining stress of 15MPa were applied, which corresponds to buried depth of 500m. For sample 3$^\#$, equal axial and confining stresses of 25MPa was applied, which corresponds to buried depth of 1000m. The triaxial stresses were first applied to samples at room temperature, which was followed by permeability measurement at room temperature. Then samples were heated up to goal temperatures from 50℃ to 600℃ in 50°C steps. Each goal temperature was sustained for two hours in order to make a uniform temperature distribution in the samples. And it

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was followed by nitrogen permeability measurement. Owing to pyrolysis-induced gas would release during heating process, permeability measurement was performed after complete discharging of gas.

3 Results

Steady flow method was used to measure permeability change in oil shale at different temperature up to 600℃. The permeability can be calculated by Darcy's law as following:

$$k = \frac{2\mu P_0 LQ}{A(P_1^2 - P_2^2)} \tag{1}$$

Where k, μ, Q, L, A are gas permeability in m^2, nitrogen dynamic viscosity at different temperatures in Pa·s, measured flow rate through sample in m^3/s, length of sample in m, and sectional area of sample in m^2, respectively. P_0, P_1, P_2 denote standard atmosphere pressure in MPa, nitrogen pressure of inlet and outlet in MPa.

3.1 Permeability evolution with temperature

Permeability of Jimsar oil shale non-monotonously evolved with temperature shown in fig.3. It can be divided into three states during heating.

Low temperature stage is the first stage which is room temperature (RT) to 200℃~250℃. In the first stage, permeability is very low and almost keep zero. It is closely related to mineral composition of oil shale. Oil shale is mainly composed of inorganic minerals (mass fraction > 90%) and organic matter (mass fraction < 10%). Fine clay minerals such as illite, smectite and kaolinite are the main components. Hence, oil shale is very tight and has low porosity at room temperature. In the viewpoint of general theory of thermal cracking, thermally induced micro-cracks would appear in the rock during heating and further augment oil shale permeability. However, for oil shale thermally induced cracks are very small in quantity due to fine mineral grains. The other thing is that thermal expansion can reduce the opening of fissures including natural fissures and thermally induced cracks. This is the reason that permeability below 200℃~250℃ is very small.

The second stage is medium temperature stage where temperature ranges from 200℃~250℃ to 450℃~500℃. Permeability increased from zero at 200℃~250℃ to approximately $3.5\times10^{-16}m^2$ at 450℃~500℃. At the beginning of this stage where temperature ranges from 200℃~250℃ to 350℃~400℃, thermal cracking in oil shale is the main reason for permeability increment. Permeability sharply rises at temperature greater than 350℃~400℃. Pyrolysis of organic matter at high temperature up to 500℃ may the main reason for permeability sharp increment.

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High permeability but small augment can be observed above 500℃. It is the final stage where temperature ranges from 500℃ to 600℃. We can also find that permeability decreases a little. In this stage, organic matter in oil shale goes into serious pyrolysis. Gas and/or oil production induced by pyrolysis can result in many considerable pores and fissures which can augment oil shale permeability. On the other hand, these newly-formed pores and fissures are compressed by triaxial stresses, which gives rise to little reduction of permeability at this stage. However, permeability still remains high level. Hence, pyrolysis can considerably augment the permeability of tight oil shale.

Permeability of tight oil shale evolving with temperature corresponds to a threshold temperature and peak temperature. The threshold temperature ranges from 200°C to 250°C and the peak temperature ranges from 450°C to 500°C. These two key temperatures divide permeability into three stages, which are very slow evolution at low temperature ranging from RT to threshold temperature, considerable increment at medium temperature ranging from threshold temperature to peak temperature and high level remaining stage at high temperature stage ranging from peak temperature to 600℃.

3.2 Effect of stress on permeability of oil shale at high temperature

Generally, stress increment results in reduction of permeability at room temperature. However, few of studies were done to reveal effect of stress on permeability of oil shale at high temperature. We performed a test on permeability evolution of sample $3^{\#}$ with temperature up to 600℃ at equal of axial and confining stresses of 25MPa that corresponds to 1000m buried depth. Like samples $1^{\#}$ and $2^{\#}$, permeability of sample $3^{\#}$ also experiences three stages shown in fig.4. However, the threshold temperature is considerably higher than that in samples $1^{\#}$ and $2^{\#}$, ranging from 350°C to 400°C. The reason may be that the opening of microcracks induced by thermal cracking is easily closed by thermal expansion and high stress. Once organic matter begins to pyrolyze at 400℃, new pores and fissures will emerge and make a big jump in permeability. The permeability can approximately reach $7\times10^{16}m^2$ at peak temperature of 500℃, which is the same as the temperature of samples $1^{\#}$ and $2^{\#}$. After peak temperature permeability exhibits a little drop but still remains a high level. Hence, pyrolysis result in high permeability of oil shale at high temperature regardless of stress state. The stress only take effect at low temperature.

4 Discussions

As mentioned above permeability evolution with temperature may be closely related to organic

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matter pyrolysis in oil shale. We measured weight loss of oil shale at temperature up to 600℃ in order to analyze effect of pyrolysis on permeability. Fig.5 shows permeability variation of sample 2# with temperature and weight loss measured by mass thermogravimetry (TG) at different temperatures. Permeability increment is listed as left axis in fig.5, which is the ratio of permeability at high temperatures (k) to that at 250℃ (k_{250}). The reason of adopting the permeability at 250℃ as baseline is that permeability can be measured only at 250℃ and is zero below 250℃. It is found that the three stages of permeability evolution, shown in fig.5, closely corresponds to three stages of pyrolysis in oil shale. At temperature below 250℃, no permeability can be measured, which is due to no pyrolysis in oil shale. Organic matter in oil shale begins to decompose and weigh loss begins to increase only at 250℃. Two sub-stages IIa and IIb of permeability can be observed at 250℃-500℃, shown in fig.5. Weight loss induced by pyrolysis can be also divided into two sub-stages. Hence, slight pyrolysis results in slow increment of permeability corresponding to sub-stage IIa. It is followed by serious pyrolysis which can give rise to drastic increasing of permeability, seen in stage IIb of fig.5. In this sub-stage, weight loss changes approximately from 99% to 90%, which increases by 9% (total about 12% within 600℃). The corresponding pyrolysis-induced permeability increases from 10 times at 400℃ to 60 times at 500℃. Weigh loss per centigrade degree slows down at above 500℃, which means that pyrolysis becomes slighter than that at 400℃-500℃. The corresponding permeability exhibits a little reduction due to stress effect but still remains a high level. Hence, pyrolysis plays an important role in permeability evolution and fundamentally changes permeability tendency and magnitude.

Gas emission during heating oil shale up to 600℃ can result in oil framework to fracture. The framework of oil shale evolves from impermeable to permeable that permeability can be improved dramatically. Hence, gas production during pyrolysis in oil shale has significant influence on its permeability. Fig.6 shows relation between gas production rate and permeability of Jimsar oil shale at different temperatures. No gas was produced at temperatures from RT to 200℃~250℃, which corresponds to the first stage of permeability change and the permeability is zero. Gas production rate increased with temperature at ~250℃ to 450℃ which corresponds to the stage pyrolysis of oil shale. In this stage, the weight loss of oil shale accounts for 90% of the total weight loss seen in fig.5. Kerogen in oil shale seriously converts to hydrocarbon gas and shale oil, which can lead to more pores and improve connectivity of pores. Hence, the increase in permeability is about 3.0×

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$10^{-16}m^2$ and it covers 89% of peak permeability. Gas production rate drops at temperature of 450℃~550℃. Permeability keeps increasing until to 500℃ then decreases at 500℃-600℃. Hence, permeability variation is closely consistent with change of gas production rate. Gas production rate reflects the intensity of pyrolysis. High gas production rate supports fast large matter loss in oil shale which can quickly produce more pores. Hence, permeability increases a lot. When gas production rate decreases, formed pores were compressed by tri-axial stresses and permeability decreases.

5 Conclusions

Based on experiments on permeability evolution of Jimusar oil shale in Xinjiang of China at high temperature and triaxial stress, the conclusions are drawn as follows:

(1) Permeability of tight oil shale evolving with temperature corresponds to a threshold temperature and peak temperature. These two key temperatures divide permeability into three stages, which are very slow evolution at low temperature ranging from RT to threshold temperature, considerable increment at medium temperature ranging from threshold temperature to peak temperature and high level remaining stage at high temperature stage ranging from peak temperature to 600℃.

(2) The threshold temperature was subjected to triaxial stresses. For Jimusar oil shale, the threshold temperature ranges from 200°C to 250°C at ground stress of buried depth of 500m and from 350°C to 400°C at buried depth of 1000m. The peak temperature was almost not subjected to triaxial stress and the range is from 450°C to 500°C for all Jimusar samples.

(3) Pyrolysis plays an important role in permeability evolution and fundamentally changes permeability tendency and magnitude. The first stage of permeability evolution is attributed to thermal expansion of minerals in oil shale. The pyrolysis causes permeability increment at the second stage. At the last stage permeability exhibits a little reduction due to stress effect but still remains a high level due to serious pyrolysis.

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References:

[1] Liu, Z.J.; Dong, Q.S.; Ye, S.Q.; Zhu, J.W.;Guo, W.;Li, D.etal.The situation of oil shale resources in China.

Peer-reviewed version available at Energies 2018, 11, 3033; doi:10.3390/en11113033

Jilin Univ(Earth Sci Ed)2006,36(6),869-876.

[2] Razvigorova, M.;Budinova, T.; Petrova, B.; Tsyntsarski, B;Kinci, E.; Ferhat, M.F.; Steam pyrolysis of Bulgarian oil shale kerogen. Oil Shale,2008,25(1),27-36

[3] Jiang, XM.; Han, X.X.; Cui, ZG; New technology for the comprehensive utilization of Chinese oil shale resources. Energy, 2007, 32(5), 772–777.

[4] Kok, M,V.; Guner, G.; Bagci, S.; Laboratory steam injection applications for oil shale fields of Turkey. Oil Shale,2008,25(1),37–46

[5] Harfi, K.E.;Mokhlisse, A;Chanaa,M.B.; Outzourhit, A.;. Pyrolysis of Moroccan (Tarfaya) oil shales under microwave irradiation.Fuel,2000,79(7),733–742.

[6] Bernabe Y.; The effective pressure law for permeability in Chelmsford granite and Barre granite.Internatioal Journal of Rock Mechanics & Mini,1986,23(3),267-275

[7] Morrow, C; Byerlee, ;Permeability of rock samples from Cajon Pass, California.Geophysical Research Letters,2013,15(9),1033-1036

[8] Zhu,W.; Wong,T.F.; Network modeling of the evolution of permeability and dilatancy in compact rock.Journal of Geophysical Research Solid Earth,1999,104(B2),2963-2971

[9] Zoback, M.D.; Byerlee, J.D.; The effect of microcrack dilatancy on the permeability of westerly granite. Journal of Geophysical Research,1975,80(5),752-755

[10] Ostensen. Microcrack permeability in tight gas sandstone. Society of petroleum engineers Journal,1983,23(6),919-927

[11] Gao,H.; Lan, Y.; Zhao,Y. et al; Chang rule of porosity and permeability of granite under high temperatur.2017 international conference on coal science & technology and 2017 Australia-China symposium on energy

[12] Feng Z.J.; Zhao Y.S.; Zhang Y.; Wan Z.J; Real-time Permeability evolution of thermally cracked granite at triaxial stresses. Applied thermal engineering. 2018, 133, 194-200

[13] Yang S.Q.; Xu, P.; Li, Y.B.; Huang, Y.H.. Experimental investigations on triaxial mechanical and permeability behavior of sandstone after exposure to different high temperature treatments. Geothermics,2017,69,93-109

[14] Zhang, Y.; Zhao, Y.S.;, Wan Z.J.;et al; experimental study on effect of pore pressure on feldspar fine sandstone permeability under different temperatures. Chinese Journal of rock mechanics and engineering,2008,27(1),53-58

[15] Niu, S.W.;Zhao,Y.S.; Hu, Y.Q.; Experimental investigation of the temperature and pore pressure effect on permeability of lignite under the in-situ condition. Trans Porous Med,2014(101),137-148

[16] Feng, Z.J.; Wan Z.J.;, Zhao Y.S.;et al; Experimental study of permeability of anthracite and gas coal masses under high temperature and triaxial stress. Chinese Journal of rock mechanics and engineering,2010,29(4),689-696

[17] Kang, Z.Q.; Zhao Y.S.; Meng, Q.R,; et a1;Micro—CT experimental research of oil shale thermal cracking

laws． Chinese J.Geophysics,2009,52(3),842-848(in Chinese)

[18] Kang, Z.Q,; Yang, D.; Zhao Y.S.; Hu,Y.Q.; Thermal cracking and corresponding permeability of Fushun oil shale. Oil shale,2011, 28(2),273-283

[19] Zhao,J.; Yang, D.; Kang Z.Q.; Feng Z.C.;A micro-CT study of changes in the internal structure of Daqing and Yan'an oil shales at high temperatures. Oil shale,2012, 29 (4),357-367

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Table 1.

Proximate analysis of Jimsar oil shale

Water (%)	0.6
Ash(%)	77.13
Volatile(%)	19.63
Fixed carbon(%)	2.64
Calorific value（cal/g）	1358

Table 2

Element Analysis of Jimsar oil shale

C (%)	15.78
H(%)	2.55
N(%)	0.4
O(%)	4.54
Total S(%)	0.35

Fig. 1 Oil shale samples

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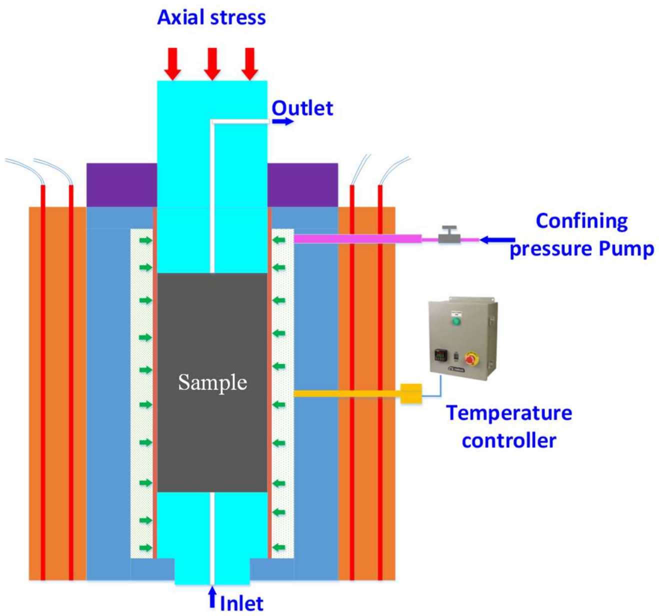
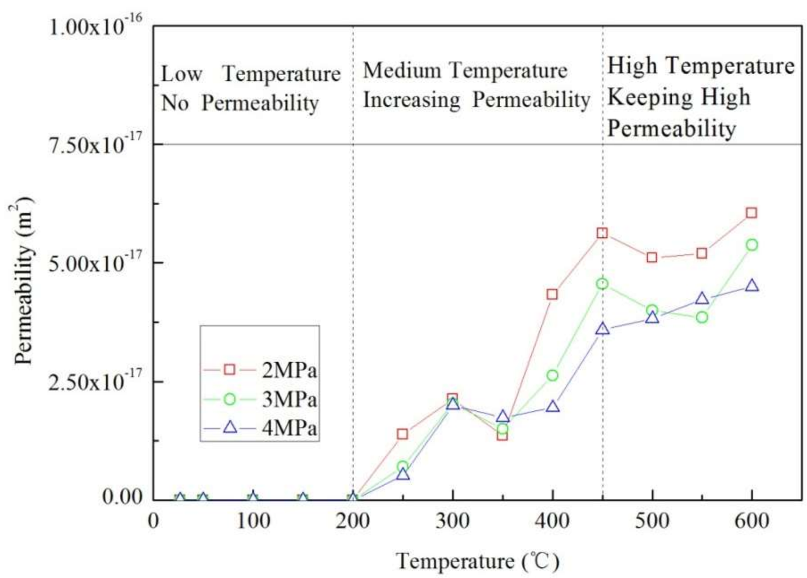


Fig.2 Schematic diagram of sample assembly



（a）1# sample

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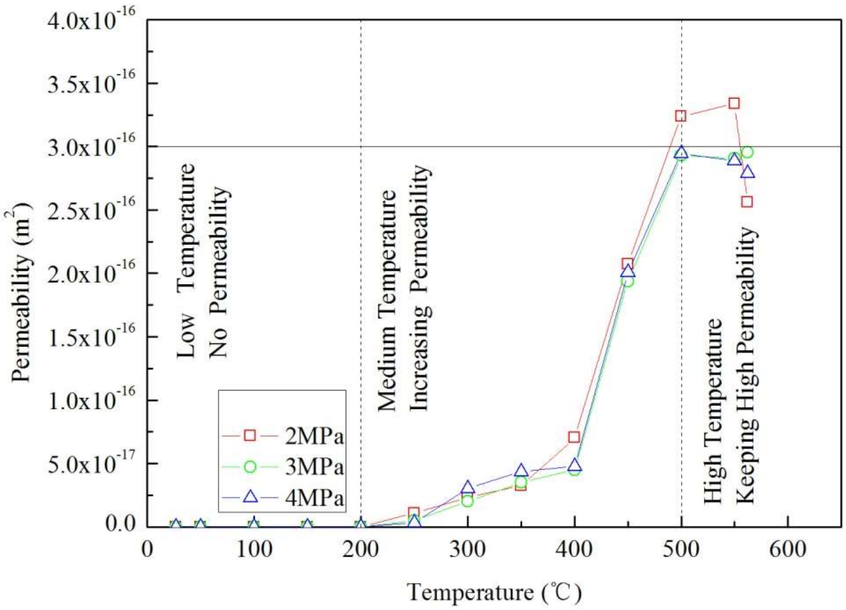

（b）2# sample

Fig.3 Permeability evolution of sample $1^{\#}$ and $2^{\#}$ at different temperatures

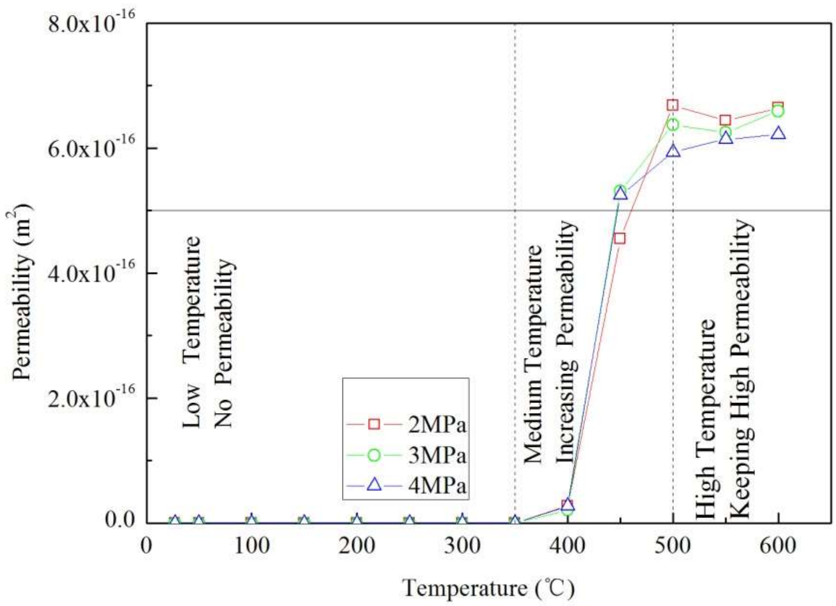

Fig.4 Permeability evolution of sample $3^{\#}$ at different temperatures

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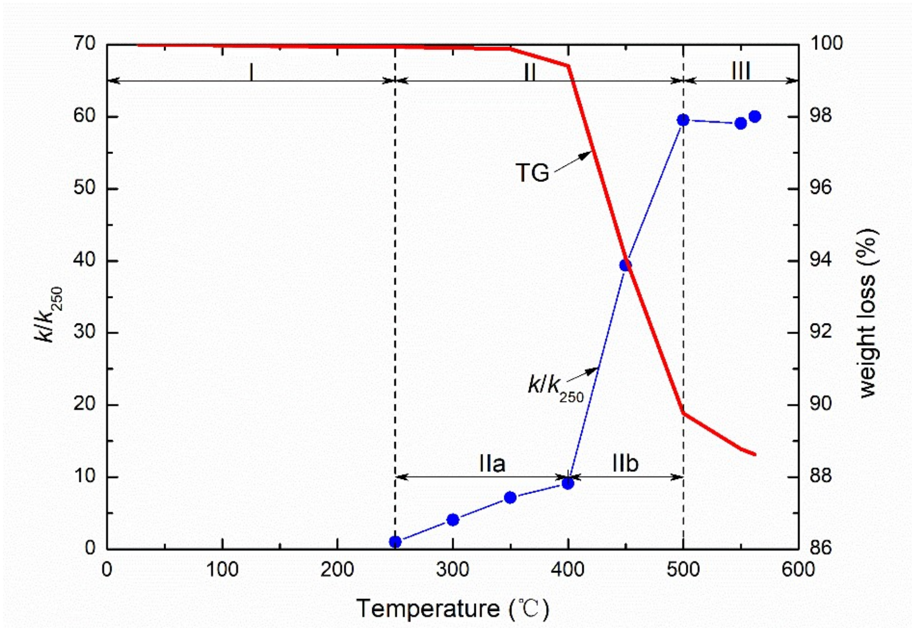

Fig.5 Comparison between permeability curve of 2# specimen and TG curve of oil shale

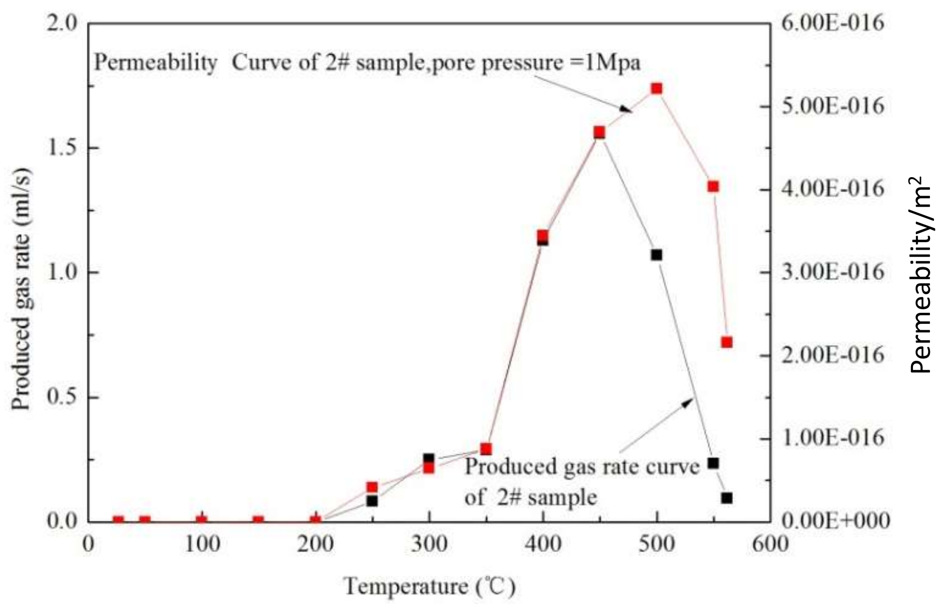

Fig.6 Comparison of permeability to produced gas rate of oil shale at temperature up to 600℃