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دراسة تجريبية حول العلاقة بين فقدان الوزن ووجود الشقوق في الصخور الزيتية

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الملخص

تم اختيار الصخور الزيتية من المنجم المفتوح في فوشون بمقاطعة لياونينغ ليتم دراسته، وتم دراسة تأثير الوقت ودرجة الحرارة على نسبة فقدان الوزن من تلك الصخور الزيتية. وأظهرت النتائج أن عرض الشق وطوله وكميته ومعدل فقدان الوزن منه يزداد مع ارتفاع درجة الحرارة، ويكون أسرع معدل للزيادة بين 400 إلى 600 درجة مئوية، ويصبح مستوى معدل فقدان الوزن ثابتاً عندما تكون درجة الحرارة أعلى من 700 درجة مئوية، مما يعني أن التغير في نسبة فقدان الوزن ليس واضحاً. في عملية الانحلال الحراري للصخور الزيتية، يوجد وقت ثابت لدرجة حرارة ثابتة (حوالي 8 ساعات). وفي ذلك الوقت، يتم ربط الشقوق الكبيرة والمتوسطة والصغيرة الحجم داخل الصخور الزيتية، وعندما يصل عدد الشقوق إلى الحد الأقصى، فإن نسبة فقدان الوزن في الصخور تصل أيضاً إلى الحد الأقصى، وهو 21.67%. ويكون الشرط للحصول على أعلى نسبة لفقدان الوزن في عينة الصخر الزيتي هو: أن تكون العينة تحت درجة حرارة تسخين ثابتة تبلغ 600 درجة مئوية لمدة 8 ساعات.

An experimental study on the relationship of the weight loss and crack width of oil shale

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Abstract

The effect of the time and temperature on the weight loss ratio of oil shale was studied. Oil shale from an open-pit oil shale mine of Fushun in Liaoning Province, China was used. The results show that crack width, length and quantity, and the weight loss rate, increase with increased temperature. The fastest increase rate was between 400 °C to 600 °C. The weight loss rate level tended to be flat when above 700 °C, which means the change in the weight loss ratio is not obvious. In the process of oil shale pyrolysis, there is an optimal constant temperature time of about 8 hours. At this time, the big, medium and small cracks within the oil shale connect. When the number of cracks reaches its maximum, the weight loss ratio of the oil shale will also reach its maximum (21.67 %). The condition for the highest weight loss ratio of the sample shale oil occurred under a constant heating temperature of 600 °C for 8 hours.

Keywords: Crack; heating time; oil shale; temperature; weight-loss ratio.

1. Introduction

Oil shale, a type of organic mineral, is a promising alternative petroleum. The in-situ mining technology for oil shale, which has been in development for years, revolves around the conversion of kerogens into shale oil by heating the underground oil shale in a variety of ways before the oil and gas come into the producing well. Although there are still many technical problems that the existing in-situ underground mining technology cannot resolve, the theoretical and technical research and the demand for environmental protection demand its continued development. The proven oil shale reserves in China are estimated at 31.567 billion tons, which means China ranks fourth in relation to the United States, Brazil and Russia (Isr. Ltd, 1992; Greg *et al.*, 1984; Wang *et al.*, 2004; Wang *et al.*, 2005; Song *et al.*, 2004**)**. Since the 1980s, in-situ heating technology has advanced along with many other technologies. Shell's ICP technology. Exxon-Mobil's Electrofrac technology, and EGL's in-situ mining technology are the most well-known m. (Kang *et al.*, 2010; Meng *et al.*, 2011).

Fissure structure is a major cause of oil shale permeability. Fissures are the main channels for seepage, making connections between numerous surrounding pores. In oil shale, fissure size is a few times to even tens of times as small as those of pores. However, the permeability of the fissure structure is higher than that of the pore structure by several orders of magnitude, and the thermal cracking inside rocks by heat is obvious. A good understanding of the role that temperature plays in the principle of oil shale thermal cracking helps engineers to make sound judgements in terms of temperature level and heating period. Consequently, in-situ oil shale mining technology costs can be reduced. The in-situ oil shale heating process will be more well guided (Pan *et al.*, 2010; Li *et al*., 2006). Therefore, it is of practical significance to study the principle of oil shale thermal cracking.

Zuo *et al*. (2015) found that thermal cracking in sandstone is mainly related to the thermal and mechanical properties of the mineral components. Thermal bursts are affected by mismatched thermal expansion and thermal expansion anisotropy, and especially by the shape of the mineral particles. Homand-Etienne and Honpert (1989) carried out a comprehensive study on granite treated by high temperature. They found that after heat treatment, the connectivity of the rock improved, and a new fracture was created. The length of a new fracture is related to a grain's shape and size. Tan *et al.* (2006) believe that after high-temperature treatment, a rock's wave velocity, permeability, porosity and other parameters will change greatly. The experimental research described in this paper was carried out using oil shale from the opencast oil shale mine in Fushun, Liaoning Province, China. The study focused on the influencing factors of oil shale weight loss.

Xue Jinxia of Shanxi Agricultural University in 2011 through experimental testing and analysis revealed the pyrolysis characteristics of oil shale. Temperature pyrolysis weight loss experiments were carried out on Fushun oil shale, and the TG and DTG curves of oil shale in the range of 20-1000°C were obtained, revealing that the Fushun oil shale has concentrated pyrolysis in the range of 330-480°C. Characteristics, weight loss about 15% of the total mass (Guégeun *et al*., 1997).

Xie *et al.* (2011) used infrared spectroscopy on the Huadian oil shale to examine raw materials and pyrolysis products. The results show that shale oil and oil shale organic matter contains similar functional groups which are mainly dominated by aliphatic hydrocarbons. However, shale oil has a higher aliphatic hydrocarbon content than oil shale. The greater the content of aliphatic hydrocarbons in oil shale, the higher the oil yield from pyrolysis. Oil shale with a low content of aliphatic hydrocarbons and a large amount of aromatic hydrocarbons has a relatively low oil extraction rate. The condensed aromatic structure of semi-coke is higher. Shale oil and oil shale organic matter contain functional groups similar to the main aliphatic hydrocarbons. They alsocontain aromatic hydrocarbons and C = O groups (Hadley, 1976; Horll & Nemat-Nasser, 1982; Xie, *et al.,* 2011). Compared to crude oil shale, shale oil has an increased fat structure and reduced aromatic structure. The aromatic structure in semicoke increases. At the pyrolysis temperature of 500 °C, oil shale organic matter is substantially pyrolyzed. As pyrolysis temperature increases, tar yield no longer increases. Secondary cracking degree also increases. Carbonate decomposition begins at 700 °C (US Department of Energy, 2007).

2. Methodology

2.1 Equipment

A muffle furnace (KSZN-k8) electronic scales, boiler dry, digital camera, pliers, and steel ruler were used for this experiment.

2.2 Samples

Samples (Figure 1) were from the open-pit oil shale mine of Fushun City, Liaoning Province, China. The specimens belong to the coal-bearing strata of the Cenozoic Tertiary, existing in a coal-rich stratum. Their appearance was dark brown, with a greasy-luster surface. The bonding formation of the rock particles was dense. Cracks were not well developed, and there was a fine primary layer. The oil content was about 8.2%.

Fig. 1. Sample of oil shale.

2.3 Experimental procedure

Before the experiment, the oil shale was processed into cuboid-shaped samples. The sample sizes were large in order to observe changes in those cracks. The oil shale samples were given serial numbers before being heated in the muffle furnace under different temperatures (100, 200, 300, 400, 500, 600 °C) for different periods of time (2, 4, 6, 8, 10 h). Each group of rock samples was weighed on an electronic balance, and their mass values were recorded after being subjected to the heating-under-constant-temperature experiment. Finally, the collected data was collated, plotted and analyzed.

2.4 Parameter measurements

More than 10 measuring points were selected per crack. Average width was measured by ruler. Each crack was measured 3 times to get the average length.

3. Data Analysis

3.1 Effect of heating temperature on oil shale weight loss ratio

Samples 1, 2 and 3 were subjected to a heating temperature of 100 °C, 300 °C and 600 °C, and the period under constant temperature for Samples 1 and 2 was 1h. The period under constant temperature for Sample 3 was 2h. The mass data obtained from the experiment are shown in Table 1. The mass of the oil shale rock samples decreased when the heating temperature increased. Figure 2 is a plot of Table 1 data. The results indicate the changes of the oil shale mass in relation to temperature.

Table 1. Rock samples at different temperatures.

	Quality Rock Samples (g)		
Temperature (°C)	No. 1	No. 2	No. 3
24	74.16	79.82	84.55
100	73.63	79.27	83.67
300	71.95	77.54	81.69
400	71.86	77.40	81.38
500	66.18	72.72	75.20
600	62.08	66.24	69.75
700	61.68	65.54	68.36

Figure 3 is a graph of the weight loss ratio in relation to temperature. The graph clearly shows that the mass of the oil shale rock decreased with the temperature increase. As the temperature increases, the process can be divided into four stages.

3.1.1 First stage: room temperature up to 300 °C

The slopes of the three curves are basically the same, and the slope is relatively small. The mass loss at this stage is mainly due to the evaporation of moisture in the oil shale. At this stage, the weight loss ratio of the rock samples is about 3%.

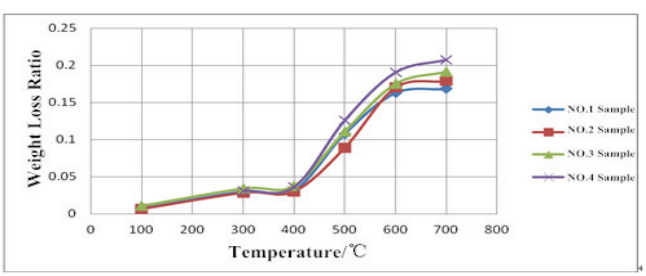

Fig. 2. Oil shale mass in relation to temperature.

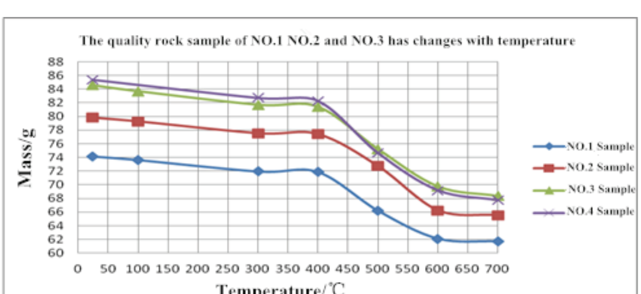

Fig. 3. Weight loss ratio in relation to temperature.

3.1.2 Second stage: 300 °C to 400 °C

The drastic of the crack width becomes gentle, and some micro cracks begin to occur around the main crack. The crack length also increases gently. The line indicating that the mass changing is almost flat, the water in the rock sample is basically evaporated to zero, the internal organic matter has not started impose, and the roto decock sample is in a transition state. The mass basically does not change.

3.1.3 Third stage: 400 °C to 600 °C

The chemical bonds with different energies in the "oil parent" of the oil shale are rapidly broken down in a very short time, resulting in a large amount of shale oil and gaseous products (CH_4, CO_2, H_2, CO, H_2S, etc.). Due to heat, the volume of these gaseous products and shale oil will instantly and rapidly expand, jetting out at high-speed, so producing a huge pressure inside the oil shale. The process occurs throughout the oil shale and produces a large number of new cracks. The lengths and widths of the previous cracks increase rapidly to form many large cracks. At the same time, many previous non-connected short cracks gradually converge to become a larger fissure. In addition, some of the cracks around the hard mineral particles a widened and extended at this temperature. The mass-indicating line drops sharply where the slope of the curve reaches a maximum between 400 °C to 500 °C. The slope starts to decrease from 500 °C to 600 °C. This shows that when the temperature reaches 400 °C, the oil shale in the organic matter begins to break down. In the beginning, it is the decomposition of light organic matter. The decomposition speed is fast, so the mass loss of the rock samples is also fast. When the temperature reaches 500 °C, the light organic matter in the oil shale is completely decomposed. After 500 °C, the heavy organic matter begins to decompose. As the heavy organic matter decomposes, more energy is needed and the decomposition process becomes more complicated. Thus, the weight loss ratio of the rock sample begins to decrease.

3.1.4 Fourth stage: 600 °C to 700 °C

The organic matter in the rock sample is completely decomposed. The indicating line tends to be flat, which means the mass is almost unchanged.

3.2 Effect of heating time on the weight loss ratio of oil shale

In the experiment, the oil shale samples were heated at 400 °C, 500 °C, 600 °C and 700 °C for different lengths of time. The maximum time under constant temperature was 10 hours. All parameters were set to observe the relationship between the oil shale weight loss ratio and temperature. The experimental data results are shown in Table 2. Figure 4 is a graphical representation of data from Table 2.

Table 2. Weight loss rate and constant temperature test data

Constant temperature (hour)	400 °C Weight loss rate	500 °C Weight loss rate	600 °C Weight loss rate	700 °C Weight loss rate
0	0	0	0	0
1	0.03065	0.0983	0.1665	0.1665
2	0.039	0.1315	0.1882	0.1817
3	0.0865	----	0.1826	----
4	0.141	0.169	0.195	0.187
6	0.1279	0.1895	0.2015	0.1981
8	0.1116	0.2319	0.2494	0.2567
10	----	0.1906	0.2147	0.2167

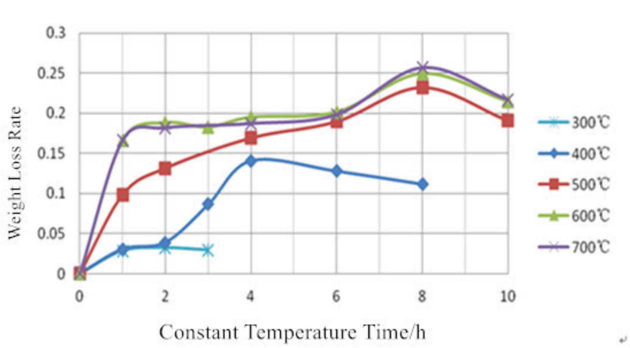

Fig. 4. Weight loss rate and constant temperature time curve.

The of this paper is on the relationship between the crack and the oil shale weight loss ratio on different heating times when the temperature is under 500 °C.

3.2.1 First stage: 2-4 h

The proportion and number of short and medium cracks reduces, and the proportion and number of long cracks increases. The weight loss ratio has a clear upward trend.

3.2.2 Second stage: 4-8 h

The proportion of short and medium cracks increases, and the proportion of long cracks decreases sharply. This may be caused by the heat transfer to the inside of the oil shale and violent thermal cracking. In addition, the cracks caused by thermal stress do not significantly change. The weight loss ratio continues to rise steadily.

3.2.3 Third stage: 8-10 h

The increase of the proportion of short and medium cracks occurs again, and the number of long cracks decreases. After the thermal decomposition, and because many small cracks develop into long cracks and the organic volatile components are substantially volatilized at this time, new small and medium cracks are seldom produced. With the heating time unchanged, the higher the heating temperature, the higher the weight loss ratio. At the same time, the difference of the weight loss ratio becomes smaller and smaller.

4. Conclusions

This experimental study focused on influencing factors on the weight loss ratio of oil shale sampled from the open-pit oil shale mine of Fushun City, Liaoning Province, China. The data shows that the main stage for water evaporation is between 100 °C to 300 °C The water content of the rock samples was about 3%. The range of 300 °C to 400 °C was the transition stage, as shown by the curve in Figure 2. The Fushun oil shale samples contained almost no decomposable organic matter. However, the main stage for the decomposition of organic matter was from 400 °C to 600 °C the organic matter content of the oil shale used in the experiment was around 14%. In the fourth stage of the heating process from 600 °C to 700 °C, practically all the organic matter in the oil shale decomposed completely. With increased temperature, the width, length and number of cracks increased accordingly, and the oil shale weight loss ratio increased in line with the changing temperature. Furthermore, the fastest increase was when the temperatures were between 400 °C to 600 °C. After 700 °C, the weight loss ratio curve generally flattens, implying slight or no changes.

The optimal period of time for heating under constant temperature in the oil shale pyrolysis process is about 8 hours. At this time, the large cracks, medium cracks and small cracks connect with each other, and the number of cracks can reach the maximum. At the same time, the oil shale weight loss ratio reaches the maximum of 21.67%.

In this experiment, the condition for reaching the maximum weight loss ratio of the oil shale rock samples under a constant heating temperature was 600 °C for 8 hours. In the actual process of in-situ mining of oil shale, there are many factors to consider. In order to obtain a higher mining rate, the flow of oil and gas should also be taken into consideration. The processes of determining the heating temperature involves various factors. These could be the focus of future research.

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