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Effect of Gelled Acid Fracturing Fluid on the Structure and Pyrolysis Behavior of Oil Shale

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Abstract: This paper simulates the application of gelled acid fracturing in the in-situ conversion of oil shale. Oil shale samples with sizes of 3-5mm were immersed in and treated with gelled acid fracturing fluid. The samples were tested by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and mercury intrusion porosimetry (MIP) before and after the acid treatment. The results show that the mineral compositions and distribution of the porosity were significantly different in the treated samples (OST) and the raw samples (OSR). SEM images show that the OST surfaces were rough and porous. The MIP analysis determined a porosity of 0.142 for the OST samples, whereas the porosity of the OSR samples was only 0.050. Thermogravimetric analysis (TGA) showed that the OST samples had a significantly higher thermal weight loss rate than the OSR samples. The Fischer assay showed that the oil yield increased from 26% to 29.2% after treatment with the acid fracturing fluid. Gas chromatography-mass spectrometry (GC-MS) analysis showed that the SNR and OST samples had different thermal decomposition kinetic parameters, the thermal decomposition activation energies at 420°C-480°C were 131KJ/mol and 127KJ/mol, respectively, which indicates that the acid treatment slightly decreased the thermal decomposition activation energy.

Keywords: oil shale, gelled acid, micropore, pyrolysis, oil yield

1. Introduction:

Oil shale is a kind of high ash sedimentary rock that contains combustible organic chemical compounds, including organic solvent-dissolvable asphaltene and undissolvable kerogen, which will produce combustible shale oil and gas upon high temperature heating[1-5]. Oil shale, which is an unconventional oil and gas resource, is an important alternative energy source. With the rising tension of the international energy landscape, oil shale has received increased attention due to its vast reserves and excellent business prospects for exploitation.

The extraction technologies of oil shale are primarily classified into two types. In the first process, the oil shale is either underground tunnel mining or open pit mining, and then directly dry distilled at the surface; this method has been widely used in China, Estonia, and Brazil. Its disadvantages include high energy consumption and high levels of environment pollution [6-9]. The second method is in-situ underground extraction; the advantages of this method include little destroying the integral structure of the underground rock mass, lower levels of pollution and low energy consumption. In-situ underground extraction will become the main means of large-scale commercial extraction in the future [7,10]. The in situ conversion

process (ICP), which is an in situ shale oil extraction technology, has been tested in the United States. Due to the low natural permeability of oil shale and the low thermal conductivity of rock mass, the increase in temperature of oil shale layers is very slow. As a result, the experiment took a long time to complete, and no desirable results were obtained [7,10].Of the different in situ shale oil extraction methods, fracturing the oil shale layers and then heating it via heat carriers is a relatively efficient method of in-situ conversion. Acid fracturing technology is a common means to increase the yield from low permeability oil fields. In addition, in recent years, acid fracturing has been widely applied in the process of large-scale shale exploitation and application, and obtained shale gas successfully.

Al-Harahsheh et al. treated oil shale with hydrochloric acid, hydrofluoric acid, acetic acid, and nitric acid for acidification and demineralization. Of the treated oil shale, those that were treated with hydrochloric acid and acetic acid had higher oil and gas yields than the untreated samples. Several studies have also described the use of acids to remove minerals in oil shale, and their results showed that acid treatment has little effect on the compositions of the organic compounds existed in the oil shale[11-15]. This paper proposes the use of gelled acid fracturing fluid to replace regular fracturing fluid for in situ extraction of shale oil. Gelled acid fracturing fluid can significantly delay the acid-shale reaction time during the fracturing process, which provides the best acidification effect. However, the effects of the gelled acid fracturing fluids on the Huadian oil shale are not clear. In the study, numerous laboratory experiments were performed to determine the effect of gelled acid fracturing fluid on the composition, structure and thermal decomposition characteristics of oil shale.

In this paper, samples of oil shale that were treated with gelled acid fracturing fluid and untreated oil shale samples were first characterized by X-ray diffraction (XRD). The results show that gelled acid fracturing fluid can effectively remove carbonate minerals from oil shale. Fourier transform infrared spectroscopy (FTIR) analysis indicated that the gelled acid fracturing fluid does not affect the kerogen components in the oil shale. Scanning electron microscopy (SEM) and mercury intrusion porosimetry (MIP) were used to characterize the porosity of these two samples, suggesting the gelled acid fracturing fluid has large influence on the oil shale's porous structure. Thermogravimetric analysis (TGA) and Fischer assays were used to analyze the effect of the gelled acid fracturing fluid on the thermal decomposition characteristics. This paper not only discusses the effect of the gelled acid fracturing fluid on the mineral composition and microstructure but also the effects on the thermal decomposition characteristics of the oil shale from the mechanistic perspective. The experiments confirmed that the treatment of oil shale with acid can decrease the compactness of the oil shale. As a result, during fracture opening, the acidification by the fracturing fluid produces additional pores, which increase the connectivity and improve the permeability of the oil shale.

2. Materials and methods

2.1 Materials

The samples were extracted from the Huadian oil field in Jilin Province, northeast of China. The samples were blocky, dark brown in color, had no special smell and did not fade. Table 1 lists the physical parameters of the oil shale samples. The samples were ground to powders by a grinding machine before use. The powders were sifted, and those with grain sizes of 3-5mm were used; these samples were called the original samples (OSR).

Table1. Physical properties of the oil shale samples

Proximate	Ultimate analysis						
(wt%, ad))			(wt%,	ad)		
Volatile	Ash	Moisture	Fixed	С	Н	Ν	S
matter			carbon				
41.9	51.8	3.9	2.4	29.2	4.3	0.6	4.9

Gelled acid fracturing fluid was used in the experiments. The primary advantage of using gelled

acid fracturing fluid is that the acid-oil shale reaction retards when making fractures. As a result, the acids can react with the oil shale sufficiently. The materials were purchased from a company in Beijing, China, and include thickener, crosslinker, gel breaker, corrosion inhibitor, and hydrochloric acid (analytical grade). Deionized (DI) water was used throughout the experiment.

The formulation of the gelled acid fracturing fluid is shown in Table 2. The fracturing fluid was prepared based on this formulation, and its performance was tested. Before the crosslinker was added, the viscosity of the base solution was very low. One minute after the crosslinker was added, gelled acid formed; the fracturing fluid had the consistency of jelly, which meets the technical requirements of carrying propping agent and fracturing the shale layer. Laboratory tests showed that at a constant temperature of 50°C, the breaking time of gelled acid can be achieved in 6 h.

Table2. Formulation of the gelled acid fracturing fluid

Hydroch	lo Thickener	Crosslinker	Gel	Corrosion
ric a	cid (wt%)	(wt%)	breaker	inhibitor
(wt%)			(wt%)	(wt%)
20	0.8	0.8	0.15	0.6

2.2 Experiments

Two sets of experiments were performed. The samples were prepared by mixing the oil shale samples with the gelled acid fracturing fluid at a solid to fluid ratio (mass of the solid to the volume of the fluid) of 1:10. The first set of experiments contained two groups (parallel samples) and was performed by immersing two 10g samples of oil shale in two 100ml of the gelled acid fracturing fluid. The second set of experiments also contained two groups (parallel samples) and was performed by immersing two100g samples of oil shale in two 1000ml of the gelled acid fracturing fluid. The conical flasks that contained the solid-fluid mixtures were placed in a water bath at a temperature of 50°C to simulate the temperature in the subsurface reservoir. In addition, the conical flasks were sealed to prevent the evaporation of the hydrochloric acid. After maintaining the conical flasks at the constant temperature for 24h, the solid-fluid mixtures were filtered to obtain the shale oil samples, which were continually rinsed with DI water until the filtrates became neutral. The washed oil shale samples were dried at 60°C in an oven for 12h to obtain the oil shale samples that were treated with gelled acid fracturing fluid (OST).

2.3 Test methods

XRD spectra was collected on a DX-2700 XRD from Dandong Haoyuan Instrument Co. (China), with Cu K α at 40kV and 30mA, scanning angles of 10°-80°, and a

scanning speed of 10°/min. Fourier transform infrared (FT-IR) spectra were recorded on a SHIMADZU IRAffinity-1 Fourier transform infrared spectrometer (Japan). The samples were prepared by finely grinding 4mg of the sample and homogenizing it with 100 mg of ground KBr (dried under an infrared lamp), and the spectra were collected in the mid-IR region from 4000 to 400 cm⁻¹. Fully automated mercury intrusion porosimetry (MIP; Auto Pore 9500, Micromeritics Instrument Co., USA) was used to characterize the porosity of the oil shale samples before and after acid treatment; the measurement range was 0.003-360.000µm. The surface structure was characterized by SEM (HITACHI S-4800, Japan) at 3kV. The SEM images were acquired at 1000, 5000, 10,000, and 30,000 times magnifications.

The oil and water that decomposed from the oil shale be determined using the low-temperature can destructive distillation test (Fischer assay). The weight of the produced gas can be calculated by subtracting the weight of the oil, water, and solid residue from the weight of the original sample. The Fischer assay was performed by heating an aluminum retort that contained the oil shale sample via resistance heating. The heating was adjusted by a Proportional-Integral-Differential (PID) temperature control system. The samples were heated to 500°C at a rate of 10°C/min and held at that temperature for 40 min. The TGA was performed on a Netzsch STA 449C thermal analyzer system (Germany). The samples were heated at a rate of 10°C/min, and nitrogen was used as the carrier gas at a flow 60ml/min. Gas chromatography-mass spectrometry (GC-MS) was performed using an Agilent7890A-5975C GC-MS (USA). Before the GC-MS, the water in the shale oil was removed by boiling an azeotrope of methylbenzene and water. The column-oven temperature was held at an initial temperature of 50°C for 5min, heated to 280°C at a rate of 10°C/min and held at that temperature for 12min; to eliminate the effect of methylbenzene on the results, the solvent delay was set at 5min.

3. Results and discussion

3.1 Change in mass of oil shale samples

Table 3 shows the mass of the oil shale samples before and after the treatment with the gelled acid fracturing fluid. During the two experiments, the mass of the samples decreased by approximately 20% after the treatment, which is mainly due to the reaction between the carbonate minerals in the oil shale (e.g., calcite, dolomite) and the gelled acid fracturing fluid. The data indicates that carbonate makes up 20% of the Huadian oil shale.

Table3. Comparison of the masses of the OSR and OST

	OSR	OST	Mass
	Mass/g	Mass/g	loss/%
First	10.05	7.82	22.18
group	10.01	7.77	22.38
Second	100.00	80.49	19.51
group	100.02	80.55	19.47

3.2 Effect of gelled acid on the composition and microstructure of the oil shale

The inorganic materials in the oil shale samples included quartz, clay, carbonate minerals and pyrite [16-18]. Figure 1 shows the XRD spectra of the OSR and OST. The XRD spectrum of the original sample (OSR) shows that quartz, illite, kaolinite, and calcite were the main minerals of the oil shale. After treatment, the calcite peaks had disappeared from the XRD spectrum.



Figure1. XRD spectra of OSR and OST samples

The FTIR spectrum of the OST sample (Fig 2) shows that the transmission peaks of kerogen at 2920cm⁻¹, 2850 cm⁻¹, and 1030-1040 cm⁻¹ are still clearly visible, which indicates that the gelled acid fracturing fluid had no effect on the organic components in the oil shale. However, the transmission peaks of the carbonate minerals at 1440 cm⁻¹ and 873 cm⁻¹ disappeared from the spectrum, which clearly demonstrates that the carbonate minerals had been dissolved and eroded by the gelled acid fracturing fluid; these experiment results further confirm the XRD results.

The SEM images show that the structures of the OSR and OST samples were significantly different (Fig 3). The SEM images of the OSR sample (Fig 3a, c) clearly show that the surface of the oil shale was smooth, the mineral particles arranged densely and orderly, and the samples contained small numbers of microcracks and small pores; the structure was dense and compact. In contrast, due to the decomposition of the carbonate minerals in the rock by the acid in the fracturing liquid, the SEM images of the OST sample (Fig 3b, d) show that a large quantity of pores had appeared on the surface of the oil shale, the minerals had become more loosely arranged, and the edges of the mineral showed curled. The surface of the shale rock exhibited a coarse and porous structure; the organic materials that had been covered by minerals were exposed.



Figure 2. FT-IR spectra of OSR and OST samples

The SEM images with a magnification of 5000 (Fig 3a, b) were processed through gray processing with MATLAB, so that the minerals and pores could be easily observed. The gray images were then converted to binary images to extract the pixels of the pores and particles. The bwarea command was used to count the points with a pixel value of 1 in the image; the area of the particles in the image was defined as $S_{\text{SEM particle}}$, and the pore area was defined as $S_{\text{SEM particle}}$, and the pore area was defined as $S_{\text{SEM pore}}$. The parameter $e_{\text{SEM}} = S_{\text{SEM particle}}/S_{\text{SEM pore}}$ was used to represent the apparent porosity of the oil shale. The values of e_{SEM} in Fig 3a and b were 0.3716 and 1.0748, respectively.



Figure3. SEM images of OSR and OST (a, c: OSR; b, d: OST)

To understand the evolution of the pores in the rock, MIP tests were performed on the OSR and OST samples. The MIP results are shown in Table 4.

Table4. MIP results

Sample	Porosity	Conter	nt of diff	ferent p	ore siz	ze (µm,
name	(%)	%)				
		< 0.04	0.04-0.	40.4-4	4-40	>40
OSR	5.0078	63.59	2.49	0.75	6.98	26.19
OST	14.2439	51.24	13.92	5.68	7.90	21.26

Table 4 shows that the total porosity of the OSR samples was 5.0078% and the total porosity of the OST samples was 14.2439%. The gelled acid fracturing fluid significantly changed the pore structure of the oil shale; the porosity increased dramatically. There was also a marked difference in the distribution of the pore sizes. The proportion of 0.04-4- μ m pores increased, whereas the proportion of pores with sizes less than 0.04 μ m decreased. These results indicate that the proportion of small pores decreased, while the proportions of medium and large pores increased. As a result, the shale rock had a more porous structure after the treatment; the connectivity improved, which benefits the transport of thermal energy and shale oil and gas.

3.3 Effect of gelled acid on the pyrolysis characters of oil shale

TGA were performed on the oil shale samples of OSR and OST. The TG curves of both samples (Fig 4) show that the thermal weight loss can be divided into three stages. In the first stage (temperatures below 200°C), the weight loss of the oil shale was mainly due to the evaporation of water vapor. In the second stage (temperatures between 200°C and 600°C), the weight loss was primarily due to the pyrolysis of kerogen in the oil shale. In addition, some of the clay minerals lost their bound water; e.g., kaolinite loses its bound water at approximately 430°C. In the third stage (temperatures 600°C 800°C), the between and derivative thermogravimetric (DTG) curves show that the weight loss peak that was present in the OSR samples was not present in the OST samples. This result indicates that the weight loss in this temperature range for the OSR samples was due to the decomposition of carbonate minerals at high temperatures. However, because the carbonate minerals were decomposed by the gelled acid fracturing fluid during the treatment process, this weight loss peak was not present in the OST samples. The DTG curves show that the weight loss rate was significantly higher for the OST samples. The temperature that corresponds to the maximum rate of weight loss remained constant at approximately 455°C.



OST samples

Fischer assays of the oil shale samples were performed before and after treatment with the acid fracturing fluid. Two parallel experiments were carried out with both the OSR and OST samples. The average values of the results are shown in Table 5. The total oil and gas yield of the OST samples increased; the oil yield increased from 19.8% to 22.5%, the gas yield increased from 6.4% to 6.7%, and the total oil and gas yield increased from 26% to 29.2%. The main reason for this increase is as follows. The carbonate minerals in the shale rock were corroded by the acid fracturing liquid, which resulted in the development of pores in the rock and increased the transport of energy and materials during pyrolysis. The higher permeability of the treated oil shale is favorable for the transport of oil and gas. These results indicate that during gelled acid fracturing process of in situ conversion, the acid would improve the porosity of the oil shale and form more connected pores, so that the oil and gas yields increased during thermal decomposition of the oil shale.

Table5. Results of the Fischer assays

Sample name OSR					OST
Weight	loss	by	gelled	acid	19.5
treatme	nt/%				
Solid residue/% 68.4					46.2
Oil/%				19.6	22.5
Water/%				5.6	5.1
Gas/% 6.4				6.7	
Total oil and gas/% 26					29.2

The analysis of the components of the shale oil from the OSR and OST samples by the Fischer assay shows that the components almost did not change; alkanes and alkenes were the main products of both samples. The GC-MS spectra (Fig 5) show that the highest abundance in the oil produced from the OSR is C_{18} , while the highest abundance in the oil produced from the OST is C_{16} . The molecular weight of the products corresponding to the maximum abundance decreased after the treatment. Overall, the low molecular weight products composed a larger proportion of the oil obtained from the OST samples; this is due to the higher porosity in the treated oil shale. As a result, the transport of energy and materials during pyrolysis increased, and the conversion of organic compounds to low molecular

weight hydrocarbons also increased. These results show the same trend as results that have been reported in the literature [13].



Figure 5. GC-MS results of shale oil from OSR and OST samples

3.4 Effect of gelled acid on the pyrolysis kinetics of oil shale

The pyrolysis kinetic parameters of oil shale can be obtained by a series of mathematical transformations of the TG curves. The detailed mathematical derivations are shown below:

$$\frac{dx}{dt} = kf(x) \quad (1)$$

$$x = \frac{m_o - m_t}{m_o - m_f} \quad (2)$$

$$k = A \exp(-E / RT) \quad (3)$$

$$\alpha = \frac{dT}{dt} \quad (4)$$

1...

where x is the conversion rate, t is time, k is the reaction rate constant, m_o is the original mass, m_t is the mass at time t, m_f is the final mass, T is the temperature, A is the pre-exponent factor, R is the universal gas constant, α is the heating rate, and E is the activation energy.

Equations (1)—(4) lead to:

$$\frac{dx}{dt} = \frac{A}{\alpha} \exp(-E/RT) f(x)$$
 (5)

Using the Coats-Redfern method and an integral transform, the equation (6) (the reaction order is 1) can be obtained:

$$-\ln\left[-\frac{\ln(1-x)}{T^2}\right] = \frac{E}{RT} - \ln\left(\frac{AR}{\alpha E}\right)$$
(6)

In equation (6), the curve of $-\ln[-\ln(1-x)/T^2]$ with respect to 1/T should be a line with a slope of E/R and an intercept of $-\ln(AR/\alpha E)$. The activation energy *E* for the decomposition of the oil shale can be obtained from the slope of the fitted line; the pre-exponent factor *A* can also be obtained [19-20].

The thermal weight loss curve of the oil shale samples (Fig 4) shows that the decomposition of the organic components mainly occurred at temperatures of 420-

480°C; the pyrolysis was most intense in this temperature range. The pyrolysis kinetic parameters were calculated for this temperature range. Figure 6 shows the curves of $-\ln[-\ln(1-x)/T^2]$ with respect to 1/T for OSR and OST samples.



Figure6. Coats-Redfern plots of OSR and OST (ECexperiment curve, FT-fitted curve)

Table6.	Kinetic parameters of pyrolysis for the oil
	shale

Sample name	E (KJ/mol)	$A(s^{-1})$
OSR	131.8	4.52×10^{8}
OST	127.7	3.71×10^{8}

Table 6 shows that in the temperature range of 420-480°C, the activation energy decreased from 131.8 KJ/mol of OSR samples to 127.7 KJ/mol of OST samples. The change of activation energy was mainly affected by two factors. Carbonate minerals play the roles of catalysts in the pyrolysis of oil shale; as a result, the corrosion and dissolution of carbonate minerals increased the activation energy. In contrast, the removal of carbonate minerals increased the porosity. Removing minerals from the organic structure decreases the energy that is required for the decomposition of the oil shale; thus, the activation energy decreased [21-22]. The calculations presented above indicate that the latter factor had a more pronounced effect on the samples that were used in this experiment.

4. Conclusions

It is clear that gelled acid fracturing fluid can erode the carbonate minerals in oil shale but does not affect the organic components in the shale. The SEM images showed that the treatment formed numerous pores on the surface of the oil shale and made the structure less compact. The apparent void ratio was as high as 1.0748. The MIP results showed that after treatment with gelled acid fracturing fluid, the porosity of the oil shale increased from 5.0078% to 14.2439%, which indicates that the microstructure of the oil shale exhibited changes on the surface but also that numerous pores formed

inside of the shale. Moreover, the connectivity of the pores improved, which increased the permeability of the oil shale. The weight loss rate of pyrolysis increased after treatment of the oil shale sample with gelled acid, and the total oil and gas yield improved. In addition, the low molecular weight products were higher in the gelled acid-treated samples. The kinetic parameters of the oil shale were calculated before and after treatment with the gelled acid fracturing fluid, and the results show that the activation energy in the temperature range of 420°C - 480°C was lower in the treated samples than in the raw samples.

During the oil shale in-situ conversion fracturing process, applying gelled acid fracturing fluid is beneficial for increasing the pyrolysis efficiency and the recovery rate of the shale oil and gas in late stages, and favorable for the transport of the produced shale oil and gas at the same time.

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