INTRODUCTION

Oil shale is a kind of representative unconventional oil resource, and the potential of shale oil production during heat treatment is predicted to be more than four times of the proved petroleum reserves of the world. Oil shale deposits of China are abundant and retorting oil shale can yield a large number of shale oil, meeting energy requirement and making it appealing for strategic reasons. However, this unconventional reservoir requires much higher technological and economic commitment from both the service sector and the producing sector to maximize the efficiency and production from these fields. Historical oil shale operations have largely been ex-situ operations by which a

Abstract

On the basis of the microwave heating method combining with hydraulic fracturing for the in-situ exploitation of oil shale, this article investigates the effects of iron oxide nanoparticles on the performance improvement of foamed pad fluid, heating efficiency enhancement under microwave irradiation and potential reservoir damage after microwave treatment. Different products were also analyzed under multiple heating parameters by using gas chromatograph-mass spectrometer (GC-MS), X-ray diffraction (XRD), and scanning electron microscopy (SEM). Heating experiments showed that foamed pad fluid was better than water based pad fluid in terms of energy conservation. Results have demonstrated that iron oxide nanoparticles can not only increase nearly 75 seconds of half-life of the foamed pad fluid, but also slightly enhance the viscosity of foamed pad fluid. Fast heating rate and energy saving were also accomplished by iron oxide nanoparticles. In the presence of iron oxide nanoparticles, it took less than 10 minutes for oil shale to reach 750°C at 1000 W, showing extremely low energy consumption. SEM experiment showed that microwave induced the creation of pores and micro fractures, and the retention of iron oxide nanoparticles inside the oil shale would not cause reservoir damage. By analyzing the products, it is recognized that reaction temperature and heating method had a great influence on the distribution of the noncondensable gases. The production of spent shale was controlled by heating method, reaction temperature, heating time, and output power. The results from this study are important to the in-situ exploitation of oil shale and environmental protection.

KEYWORDS
foamed fracturing fluid, in-situ exploitation of oil shale, microwave irradiation, nanoparticles
large amount of pollution could be made, so in-situ exploitation methods are under active development.3,4

Among in-situ exploitation methods, microwave irradiation can be a promising and potential technique for heating oil shale. Based on a wellbore radiating antenna, microwave, less influenced by reservoir geometry, heterogeneity, and properties, is capable to distribute energy over a large reservoir volume with more efficiency and better environmental protection. Many researchers have demonstrated the possibility of microwave heating for the pyrolysis of oil shale as well as the recovery enhancement of heavy oil. Neto et al5 applied a zeolite-based catalyst for cracking produced shale oil into lighter liquid samples under microwave irradiation. A novel tight-shell installed with microwave emitter was designed for thermal heavy oil at laboratory scale, showing better temperature distribution along the distance from the antenna.6 To understand the applicability of microwave heating on heavy oil recovery, Bientinesi7 conducted a pilot scale microwave experiment, demonstrating that the temperature of the heavy oil sample was higher than water boiling point.

Although achievements were confirmed by many studies, two key factors should not be ignored for the in-situ exploitation of oil shale under microwave heating. One is that oil shale is weak in wave absorbing and another is that oil shale is a kind of shale rock with low porosity and permeability.8 Bregar9 confirmed the function of ferromagnetic nanoparticle as microwave absorbent by analyzing the magnetic properties of nanosize ferromagnetic particles. Bera and Babadagli10 held that activated carbon and nano-metal oxides could be used to make the microwave processes faster. Similarly, carbon nanocatalyst was used to irreversibly reduce the viscosity of heavy oil after microwave heating.11 Another investigation on microwave heating efficiency enhanced by nickel and iron nanoparticles was published by Bera and Babadagli. They measured the viscosity reduction in heavy oil under different power levels and different concentrations of nanoparticles.12 However, nanoparticles they used in the lab were in the form of powders and the injection of nanoparticles was usually neglected. To solve this problem, Greff and Babadagli proposed that nanofluids can be injected at different stages of microwave heating,13 although the aqueous dispersion ability of nanoparticles is a huge challenge because nickel and iron nanoparticles are easy to settle and aggregate together in water. It should also be noted that nanoparticles would efficiently work as absorbent after all the liquid evaporates out of the heating system under microwave heating.

Another challenge could be overcome by a common-used stimulation method called hydraulic fracturing aimed to enhance effective permeability of reservoir.14 Hydraulic fracturing stimulation treatment can crack the formation and propagate fractures, and thus improves the seepage channels of produced oil and gas. As early as 1967, Miller and Howell15 successfully used liquid nitroglycerin to increase the permeability of oil shale reservoir. Chen et al16 from Jilin University proposed in-situ fracturing-nitrogen method to enhance the permeability of oil shale and filed experiment was successfully conducted to speed up heating rate of oil shale. As a result, combining with above two solutions, fracturing fluid could meet the requirements of the nanoparticles injection and seepage channels improvement. That is to say, fracturing fluids can not only create fractures, but also can carry nanoparticles.

In the past few years, numerous attempts applying nanotechnology in the oil industry have been made in enhanced oil recovery,17 borehole geophysical measurements18 and fine migration prevention.19 Furthermore, nanoparticles can stabilize aqueous foams in terms of delaying foam drainage, coalescence, and coarsening.20,21 Studies have shown that nanoparticles-surfactant-stabilized foam as a fracturing fluid has better performance in proppant carrying capacity.22 Fei et al reported the synergistic effect between the surfactant and silica nanoparticles on foam stability under high temperature23 and numerical simulation was also analyzed to successfully confirm this study.24 Therefore, foams carrying nanoparticles could also be stabilized by nanoparticles conversely. Pad fluid, slurry fluid and displacing fluid consist of three fluids that pad fluid does not carry proppant but creates main fractures.25 According to the relative low performance requirement of pad fluid, nanoparticles are suited to be mixed with foamed pad fluid and pumped together into the formation. Base on above investigations and researches, the aqueous dispersion of iron oxide nanoparticles in this study was used to enhance the heating efficiency of microwave irradiation and stabilize foamed pad fluid at the same time.

The main objectives of this study are devoted to investigating whether iron oxide nanoparticles affect the performance of foamed pad fluid and foamed pad fluid stabilized by iron oxide nanoparticles could be used as working fluid to enhance the heating efficiency of microwave heating without extra reservoir damage. At last, the transformation products of oil shale under different heating parameters were analyzed to significantly understand the mechanism of transformation processes.

2 | MATERIALS AND METHODS

2.1 | Preparation of aqueous dispersion of iron oxide nanoparticles

The aqueous dispersion ability of nanoparticles is a world challenge for researchers. In order to reduce this negative effect, the aqueous dispersion of iron oxide nanoparticles was prepared by the coprecipitation of Fe3+/Fe2+, using sodium hydroxide as the precipitating agent to adjust the pH value.
of 11. Four water ferrous chloride, six water ferric chloride, sodium hydroxide, polyethylene glycol (PEG), and deionized water were of analytical grade and used without further purification. Specifically, a layer of protective film on the surface of iron oxide nanoparticles can be formed by PEG to prevent iron oxide nanoparticles from settlement and aggregation.

### 2.2 Sample characterization and observation

The oil shale chosen for this study was originated from Maoming, Guangdong Province, China. The blocky oil shale was prepared by grinding and sieving to a particle size range of 3-8 mm with standard sieves for microwave heating experiments. Another part of samples crushed and sieved by 60-100 mesh sieve were used to prepare artificial cores with a diameter of 2.54 cm. The characteristics of Maoming oil shale are shown in Table 1. Particularly, a Fischer assay experiment was conducted under anoxic condition, and all production data after heating was analyzed based on an as-received basis.

A stereo microscope (XLT-165; Jiangxi Phoenix Optical Technology Co., Ltd, China) equipped with color camera was used to acquire the images of oil shale surface. The working distance is from 3 cm to 16 cm. The oil immersion objective lens of 4.5× with continuous variable times and the eyepiece of 10× were used for magnification. The stage and movement of the microscope are controlled by horizontal and vertical support. Furthermore, scanning electron microscopy (SEM) equipped with energy dispersive spectroscopy (EDS) was conducted to observe the retention of iron oxide nanoparticles inside the core and analyze the minerals of oil shale before and after microwave irradiation. Samples were firstly prepared to be conductive by surface treatment. After being sputter-coated with gold, every sample was placed in the vacuum chamber of scanning electron microscope (Quanta 450, FEI, USA) with maximum magnification lenses of 100 000×.

### 2.3 Preparation and characterization of foamed pad fluid

Fracturing fluid is made up of pad fluid, slurry fluid and replacement fluid. Pad fluid pumped into formation is applied to crack the formation and propagate fractures. In this study, foams stabilized by iron oxide nanoparticles were considered as foamed pad fluid. Similarly, apart from creating fractures, foamed pad fluid was applied to carry iron oxide nanoparticle and pumped together into the deep formation.

In order to prevent iron oxide nanoparticles from settlement and aggregation, the base fluid of foamed pad fluid was prepared by mixing 0.25 wt% sodium dodecyl sulfate with aqueous dispersion of iron oxide nanoparticles. The Warning Blender method was applied to prepare the foamed pad fluid. A 100 mL base fluid was stirred for 1 minute at 8000 rpm using a blender (GJ-3S; Qingdao Senxin Machinery Equipment Co., Ltd, China). Once foamed pad fluid was well-prepared, it was transferred to a sealed cylinder to record the foam volume and half-life. Moreover, the viscosity of foamed pad fluid with and without iron oxide nanoparticles was investigated under the shear rate of 170 second−1 using a rheometer (HAAKE MARS III, Thermo Scientific, Germany). Core flooding experiment was conducted by a displacing apparatus in the laboratory to analyze the permeability damage caused by injecting the base fluid of foamed pad fluid. Specifically, the base fluid of foamed pad fluid was injected into the core holder to investigate whether pores would be blocked by iron oxide nanoparticles. The retention of iron oxide nanoparticles in the core was observed by SEM before and after microwave treatment at an output power of 800 W within 30 minutes. All above experiments were used to evaluate the performance of foamed pad fluid in the presence of iron oxide nanoparticles.

### 2.4 Apparatus and methods

Based on the microwave heating method for the in-situ exploitation of oil shale proposed by our previous study, we further investigated the release of noncondensable gases from oil shale at different temperature stages (350-450°C, 450-550°C, 650-750°C, after 750°C) under microwave heating at an output power of 800 W. For each experiment, about 50 g sample of oil shale with 2.5 mL of base fluid containing 0.1 wt% iron oxide nanoparticles was irradiated in a microwave apparatus with a maximum output power of 1600 W. According to our previous experience, the liquid of the base fluid would firstly be heated and evaporate out of the heating system, and then iron oxide nanoparticles would further enhance the heating efficiency of microwave heating. Microwave emitting sources, microwave cavity, production discharging system and data collecting system consist of microwave experimental apparatus shown in Figure 1. In
order to realistically simulate the heating process, there are several small holes (diameter of 0.25 cm) in the bottom of sample container made up of quartz. Two ports are in the top of the container at the same time. The upper tube on the left is 320 mm in length with an inner diameter of 11 mm, while the lower tube is 175 mm in length with an inner diameter of 7 mm. The sample temperature was measured by K-type thermal couple inserted in the upper tube on the right. Gas discharged from apparatus during microwave irradiation was collected by vacuum bag after condensation. The volume of the noncondensable gases was measured by gas flow meter. The total heating time was 30 minutes. If the oil shale reached the set point in less than 30 minutes, the temperature in the reaction cavity would remain unaltered. After heating experiments, the weight of the remaining solid was measured. In addition, about 50 g sample of oil shale was also heated in an electric oven. Experimental conditions were the same as microwave experiments. And all of the experiments were not conducted under anoxic condition, because there is no guarantee that oxygen does not exist in the reservoir during the development of oil shale.

2.5 | Product analysis

The kerogen inside the oil shale would transform into oil and gas when the temperature arrives at the decomposition temperature of kerogen. The noncondensable gases at different temperature stages (350-450°C, 450-550°C, 550-650°C, 650-750°C, after 750°C) were collected in vacuum bag at an output power of 800 W and the volume of the gases were measured using a gas flow meter. The GC-MS (SQI, Thermo Fisher, USA) was performed to analyze the content of hydrocarbons (C₁, C₂, C₃, C₄, C₅, C₆) and sulfurous gases at different temperature stages. The chromatogram was obtained by capillary chromatographic column to separate the components of different mixture while mass spectogram was obtained by collecting molecular weight. By combining chromatogram with mass spectogram, the content of all volatile gas components can be acquired. Spent shale under different microwave heating time (10, 20, 30 minutes), reaction temperature (550, 650, 750°C) and output power (600, 800, 1000 W) was analyzed by X-ray diffraction (XRD; D8 ADVANCE, Bruker, Germany) to investigate the changes of minerals and clay minerals before and after heating. Specifically, SEM equipped with EDS was conducted to confirm the results of component analysis.

3 | RESULTS AND DISCUSSION

3.1 | Properties of foamed pad fluid with iron oxide nanoparticles

Hydraulic fracturing has helped in increasing the production of hydrocarbon and thus makes a significant contribution to the oil and gas industry, especially to the unconventional resources. The seepage of oil shale can be highly improved by hydraulic fracturing. The fracturing fluid is pumped into the reservoir with a pressure to crack the formation, among which pad fluid is injected to create and propagate the fractures and serves as a cooling agent for the rock face. Also, in order to meet the heating requirement, it’s important to choose suitable pad fluid.

Figure 2 shows the temperature distribution of oil shale at the first 5 minutes of heating time. It can be seen that more water containing the same amount of nanoparticles (0.1 wt%) would lead to longer time of stage 2 because water would firstly evaporate under microwave exposure. This phenomenon can be
explained by that water absorbed most of microwave because of its high dielectric loss corresponding to stage 1. Then when temperature reached approximately the boiling point of water, the heating rate reduced corresponding to stage 2. Finally, when most of water evaporated and was further discharged out of the heating system, the heating rate increased again corresponding to stage 3 due to the existence of iron oxide nanoparticles. As a consequence, too much water will inevitably lead to unnecessary waste of energy. Foamed pad fluid can not only reduce the filtration of liquid, but also contain less water which is more suitable as a working fluid for microwave heating. Although developing oil shale faces many challenges such as low permeability, clay swelling and migration, formation complexity and heterogeneities, foamed pad fluid resulting in better water control and stabilization benefits the transportation of iron oxide nanoparticles and energy conservation.

When investigating the effect of iron oxide nanoparticles on the performance of foamed pad fluid, Figure 3 indicating an increase in half-life of the foams shows that more stabilized foamed pad fluid can be acquired by
iron oxide nanoparticles. Specifically, in the presence of iron oxide nanoparticles, the half-life of the foamed pad fluid could be enhanced by about 75 seconds. Many studies revealed that foams can be stabilized by surfactant-nanoparticle mixture. Nanoparticles in the foam system play a role in preventing foams from drainage, coarsening and coalescence. Although Figure 3 shows that there is little difference in the foam volume when adding different concentrations of iron oxide nanoparticles, the half-life is highly enhanced especially by 0.1 wt% concentration of iron oxide nanoparticles. The viscosity behavior is very important to the performance of foamed pad fluid such as stabilization and filtration property. Pad fluid in the fractures is under shear force with the shear rate approximately ranging from 20 to 200 second$^{-1}$. Foamed pad fluid with low viscosity under shear force shows that foams are easy to break. Unstable foamed pad fluid is detrimental to creating fractures and carrying iron oxide nanoparticles into the formation deeper. And uneven distribution of iron oxide nanoparticles inside fractures may also lead to unexpected heating result, showing the importance of aqueous dispersion ability of nanoparticles. The change in the apparent viscosity of foamed pad fluid with and without 0.1 wt% iron oxide nanoparticles under different shear rate is shown in Figure 4. The test temperature was controlled at 30°C. The shear rate changed from 0 to 200 second$^{-1}$. At first, almost 0 second$^{-1}$ shear rate corresponded to very high absolute viscosity, which represented that foamed pad fluid were not sheared. As with shear rate increased, foamed pad fluid showed obvious shear thinning behavior because of the rupture of foams. The viscosity of foamed pad fluid with iron oxide nanoparticles was a little higher than that of foamed pad fluid without iron oxide nanoparticles, but two kinds of foamed pad fluids at last showed the same viscosity corresponding to 80 mPa·second which is enough to carry iron oxide nanoparticles.

Core flooding test was based on a comparison between the core permeability before and after injecting the base fluid with 0.1 wt% iron oxide nanoparticles which was kept inside the core for 2 hours. The damage rate was calculated as follows.

$$\eta_d = \frac{k_1 - k_2}{k_1}$$  \hspace{1cm} (1)

where $\eta_d$ is the damage rate caused by injecting the base fluid with 0.1 wt% iron oxide nanoparticles, %; $k_1$ is the initial core permeability, $\mu$m$^2$; $k_2$ is the core permeability after injecting the base fluid with 0.1 wt% iron oxide nanoparticles which was kept inside the core for 2 hours, $\mu$m$^2$.

Specifically, $k_1$ and $k_2$ were averaged when there were few fluctuations in the permeability data. The variation in the core permeability before and after the test shown in Figure 5 indicated that iron oxide nanoparticles hardly blocked the pores and caused much damage. SEM experiments confirmed this conclusion. Before core flooding, there are several pores and cracks in the artificial core as shown in Figure 6A. After displacing the base fluid with iron oxide nanoparticles into the artificial core, the surfactant obviously stuck to the surface of the pore and iron oxide nanoparticles absorbed on the surface of the surfactant due to their high specific surface area (Figure 6B). This conclusion was supported by the EDS result, showing
the existence of element of Fe, C, and O. Although the absorption of surfactant and iron oxide nanoparticles would slightly reduce the permeability as shown in core flooding result, there was not the creation of big blockage. Moreover, it is important to investigate the retention of iron oxide nanoparticles inside the core after microwave irradiation which would be discussed later since microwave heating may influence the pore structure and create micro fractures.30,31

On the whole, it can be seen that the foamed pad fluid with iron oxide nanoparticles can meet the requirements as the working fluid during fracturing treatment and the retention of iron oxide nanoparticles has little effect on core permeability. However, the deep understanding of stabilization the mechanism of foams with nanoparticles is needed for the future research and this is beyond the scope of this article.

3.2 | Heating behavior

Microwave heating, different from heat convection or heat conduction, can heat samples internally regardless of the physical contact between the microwave source and the sample. Since most of the minerals consisting of oil shale are weak microwave absorbents, oil shale can hardly absorb microwave.32 This shortcoming can be overcome by adding chemicals with high microwave absorption. Iron oxide nanoparticles could be a good option which is proved by Hasçakir’s research.33 Figure 7 shows the temperature distributions of all experiments with different output power in the presence of iron oxide nanoparticles. In our previous study,34 temperature result showed that 0.1 wt% concentration of iron oxide nanoparticles could meet the requirement of fast heating rate, so 0.1 wt% iron oxide nanoparticles were used in all microwave experiments. For microwave irradiation, high
output power accelerated the movements of molecules and further promoted the energy conversion from kinetic energy to heat energy, especially for the material with high dielectric loss. Specifically, the time reaching the set point of 750°C reduced when output power increased, demonstrating that the temperature distribution was affected by microwave absorbent as well as output power. Furthermore, the same amount of oil shale was also heated in electric oven. More heating parameters are shown in Table 2. It took about 55 minutes for the electric oven to reach the set point of 750°C at extremely high output power. The energy consumption of microwave heating was less than one hundred times the energy consumption of electric heating, showing great potential in the in-situ exploitation of oil shale in terms of time saving and energy conservation.

After core flooding test, the core was also heated under microwave irradiation at an output power of 800 W and an ultimate temperature of 750°C within 30 minutes. Figure 8 shows the three different stages (original sample, sample after core flooding, sample after microwave heating) of oil shale observed by the microscope of 10 times magnification. There was little difference before and after core flooding (Figure 8A,B) while there was a huge change in the morphology and structure of oil shale after microwave irradiation (Figure 8C). More pore space was created during the heating process and the core even crushed. Many small fractures could also be seen in Figure 8C. Organic matter called kerogen under high temperature transformed into oil and gas, remaining a large number of pores.35,36 Besides, microwave exposure induced the growth of micro fractures inside the core due to differential thermal stress within oil shale matrix.37 Unfortunately, the degree of permeability enhancement could not be measured because of the collapse of oil shale sample.

Core sample after heating was also analyzed to investigate the retention of iron oxide nanoparticles inside the core. The surfactant could not be seen in Figure 9B, showing that the temperature was so high that the surfactant decomposed completely. In addition, there are many particles bigger than iron oxide nanoparticles on the surface of minerals and clay minerals shown in Figure 9D. Table 3 summarizes the element composition of these particles determined by EDS on the surface after microwave irradiation. A large distribution of Fe and the existence of K, Al, Si, Na demonstrated that the particles of minerals and clay minerals may wrap the iron

![FIGURE 7](image_url)

**TABLE 2** Heating parameters information about oil shale

| Heating method      | Output power (W) | Temperature (°C) | Time (s) | Energy (kJ) | Normalized value |
|---------------------|------------------|------------------|----------|-------------|-----------------|
| Microwave heating   | 600              | 750              | 1800     | 1080        | 0.003           |
| Microwave heating   | 800              | 750              | 1800     | 1440        | 0.004           |
| Microwave heating   | 1000             | 750              | 1800     | 1800        | 0.005           |
| Conventional heating| 100 000          | 750              | 3960     | 360 000     | 1               |
oxide nanoparticles resulting from the physical and chemical reactions of minerals and clay minerals at high temperature. In Figure 9C, large pores and fractures are not blocked by these particles, so the retention of iron oxide nanoparticles after microwave exposure has little impact on the seepage channels of produced oil and gas.

3.3 | Products analysis under different heating parameters

Heat treatment of oil shale can yield a number of petroleum products useful as transportation fuels and materials for petrochemical industries. Liquid hydrocarbons called
shale oil are used to produce gasoline, kerosene, and paraffin wax after processing operation. Gaseous products can be applied as fuel for heating after desulphurization and hydrogenation, and remaining ash is able to manufacture building cement and chemical products. Microwave heating is more advantageous in oil quality than conventional heating in terms of light hydrocarbons and the content of sulfur. More details of the results and analysis can be found in our previous study.

Fast heating rate led to intense gas release, benefiting the creation of micro fractures because of the elevation of local pressure. The release of noncondensable gases such as hydrocarbon and sulfurous gases was studied at different temperature stages (350-450°C, 450-550°C, 550-650°C, 650-750°C, after 750°C) at an output power of 800 W. Gas production was determined based on the initial amount of original sample and was calculated as follows:

\[
\text{Gas volume yield} = \frac{V_{\text{gas}}}{M}
\]

where \(V_{\text{gas}}\) is the volume of gas release calculated by gas flow meter, mL, \(M\) is the mass of the oil shale, g.

Figure 10 compares the gas chromatography-mass spectrometry (GC-MS) analysis of non-condensable gases under different heating parameters. The relative intensity of the MS spectrum was estimated according to the area ratio of a peak to the largest peak in the spectrum. The components in hydrocarbons can be categorized as C1, C2, C3, C4, C5 and C6 according to the number of carbon atoms in the compound. These hydrocarbons contained both saturated and unsaturated hydrocarbons. Figure 11 compares the release of hydrocarbons in the noncondensable gases at different temperature stages during microwave and conventional heat treatment. The hydrocarbons production of microwave heating was absolutely higher.

**FIGURE 10** GC-MS spectra of the non-condensable gases under different temperature stages: (A) microwave heating and (B) conventional heating
than that of conventional heating, though the percentage of C_1, C_2, C_3 for conventional heating accounted for the most of the production. For conventional heating, when temperature exceeded 650°C, there was too little gas to collect and analysis. The production of hydrocarbons from 350 to 450°C is the least for microwave heating and the most for conventional heating resulting from the great difference of heating rate. When temperature was higher than 350°C, oil shale had already begun to decompose. It took about 8 minutes for conventional heating to reach 450°C from 350°C while it took about 1 minute for microwave heating. So reaction time plays a vital role in hydrocarbons production at different temperature stages. For microwave heating, the production of hydrocarbons increased at first, then decreased and at last increased again with the an increasing temperature. Actually, chemical reactions are the most intense between 450 and 650°C. After that, gas release slowly reduced but the content of hydrocarbons was the most after 750°C due to the relatively long reaction time within 30 minutes.

The release of sulfur compounds in the non-condensable gases at different temperatures is shown in Figure 12. Sulfur compounds were derived from H_2S, COS, CH_4S in the non-condensable gases, and the content of H_2S was a large portion of the total. Figure 12 indicates that heating method has a great impact on the distribution of sulfur compounds. The release of sulfur compounds for microwave heating was extremely higher than that for conventional heating. Several studies have revealed that shale oil obtained by microwave heating contains less content of sulfur, indicating that more sulfur was released in term of gas due to the break of chemical bonds under microwave irradiation. Although it takes less than 4 minutes from 450°C to reach 650°C, the release of sulfur in terms of gas is relative high at 450-550°C and 550-650°C temperature stages shown in Figure 12, because the decomposition of the majority of pyrite takes place between 450°C and 650°C. After all the liquid and gas products released from the raw oil shale, there was only solid remaining in the reactor called spent shale. It is essential to figure out the physical and chemical changes of spent shale during heat treatment because the properties of it also influence the exploitation process. Figure 13 reports the variations in yields of spent shale under different reaction temperature, reaction time and output power. It can be seen that spent shale production was mainly affected by reaction temperature and heating time, while there was little difference for output power. However, heating time barely influenced the spent shale production for electric heating, since microwave with rapid heating rate could induce some complex chemical reactions at high temperature. Apart from the transformation of organic matter, minerals, and clay minerals were also under alteration and decomposition. The raw oil shale and spent shale were all characterized in Table 4 with the XRD analysis, showing that the major components of raw and spent shale were both clay minerals and quartz while feldspar, calcite, and pyrite accounted for a small portion of samples. During microwave irradiation, the percentage of quartz increased while the percentage of some minerals and clay minerals reduced mainly resulting from the thermal stabilization of quartz and the thermal decomposition of some minerals and clay minerals. Specifically, the content of pyrite decreased but the siderite came into being which should be a comprehensive result from the factors including the different complicated reactions at high temperature, the existence of iron oxide nanoparticles and the peculiar heating method.
dielectric property accompanying with high wave absorbing, so pyrite distinctly underwent structure change (Figure 14B), component decomposition and surface cracking (Figure 14C).

Product analysis shows that microwave accelerates heating rate, induces more complicated chemical reactions and leads more decomposition of minerals and clay minerals. It is undeniable that output power and heating time are also the influential factors in the production of spent shale. Although it is beyond the scope of this paper, it is necessary to investigate the mechanical properties of spent shale.

4 | CONCLUSION

Since new discoveries for conventional oil and gas reservoirs have been declining steadily over the past few decades, the rising energy demand has imposed increasing interests in exploiting oil shale without causing extra contamination. Microwave heating method combining with hydraulic fracturing in the presence of iron oxide nanoparticles has the ability to develop them to the maximum potential. Based on this novel method, the application of iron oxide nanoparticles mixed with foamed pad fluid was studied in terms of enhancing the performance of foamed pad fluid and increasing the heating efficiency for oil and gas production under microwave irradiation. The half-life of foamed pad fluid stabilized by iron oxide nanoparticles could be increased significantly and the viscosity also meets the requirement of pad fluid. The retention of iron oxide nanoparticles inside the core before and after microwave exposure would not block the pores of oil shale shown in SEM images, corresponding to the permeability damage result. On the contrary, more pores and micro fractures were created by microwave heating because of the transformation of kerogen and the thermal stress. Heating experiments have indicated that foamed pad fluid is more suitable than water based pad fluid in terms of energy conservation. In the presence of iron oxide nanoparticles, fast heating rate and the transformation of oil shale were efficiently
accomplished by microwave heating. Moreover, the release of hydrocarbons and sulfur gases influenced by reaction temperature is more intense and complex than that of conventional heating. At last, minerals and clay minerals underwent structure change, component decomposition and surface cracking during microwave irradiation and thus endured the extra loss of weight.

Although the unique functions of iron oxide nanoparticles make it possible to efficiently in-situ develop oil shale under microwave heating combining with hydraulic fracturing, more investigations such as the mechanism of foam stabilization by nanoparticles and the mechanical properties of spent shale after microwave exposure are required in the future. Notwithstanding the existence of above challenges which have
not been overcome, iron oxide nanoparticles show excellent potential in helping microwave heating in-situ develop oil shale.

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CONFLICT OF INTEREST

The authors declare no competing financial interest.

AUTHOR CONTRIBUTIONS

Jingyi Zhu and Zhaozhong Yang conceived and designed the study. Jingyi Zhu and Shuangyu Qi performed the experiments. Jingyi Zhu wrote the paper. Jingyi Zhu, Zhaozhong Yang, Xiaogang Li, and Min jia reviewed and edited the manuscript. All authors read and approve the manuscript.

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**SUPPORTING INFORMATION**

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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