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EFFECT OF IN-SITU COMBUSTION PROCESS ON THE MAGNETIC PROPERTIES AND COMPOSITION OF ROCK

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Abstract

In-situ combustion (ISC) is a proved, effective method for enhanced oil recovery (EOR). In our previous work, we studied the feasibility of ISC process for heavy oil recovery in Nurlat Oil Field (Tatneft oil company, Russia) regarding to oil recovery, in-situ oil upgrading, stability of combustion front, etc. In this work, we investigated the effect of ISC process on the rock properties and composition. We found that magnetic minerals can be in-situ formed in rock during combustion process of oils. The formation of magnetic minerals in rock depends on temperature, heating time, and oil environment. Based on the magnetic properties, the samples can be divided into the most heated, less heated, and non-heated ones with hydrocarbons. The changes in the magnetic properties of rock can be used for developing technologies for combustion front monitoring, which is very valuable for controlling ISC process and its adjustment.

Keywords:
Magnetic properties;
Thermomagnetic analysis;
Enhanced oil recovery;
In-situ combustion;
Rock.

1. Introduction

As a proved, efficient enhanced oil recovery (EOR) technique, in-situ combustion (ISC) has a history of about a hundred year [1]. In recent years, it has been attracting more and more attentions due to its high efficiency, easily accessible injectant (air), and environmentally friendly properties, especially for heavy crudes recovery (heavy oil, bitumen, oil shale, etc.) [2,3]. In spite of these advantages, ISC technique has not been as widely implemented for EOR in the field as steam injection process. The main challenge is its complexity, which makes it difficult to predict, control, and adjust [4,5].

To increase its predictivity and controllability, many researches have been carried out from different aspects, such as: studies on the combustion of different types of oils, their SARA fractions, as well as pure hydrocarbons (alkanes, aromatics, etc.) to understand the complex combustion mechanism [6–13]; studies on the factors affecting the ignition as well as the establishment and propagation of combustion front, including reservoir temperature, pressure, rock composition, and water saturation, etc.[14–18]; the effect of catalysts on the combustion behavior of oils and the performance of ISC process [3, 6, 19-23]; and numerical simulation studies to optimize injection parameters and to predict the displacement efficiency and economic benefit [24–29]. These researches can help to understand the combustion mechanism and EOR mechanism, as well as to predict the efficiency of ISC process. However, the current studies and techniques fail to know where is the combustion front and how it is propagating once the combustion front is established in field application of ISC process. In this work, we investigated the effect of combustion process of heavy oil on the composition and magnetic properties of rock. In fact, recently we have found that changes in magnetic properties can give answer about the movement of combustion front [30]. By doing this, we can provide fundamental data for developing new techniques that can help to monitor combustion front on the ground.

2. Experimental Section

2.1. Materials

Initial rock sample was provided by the Nurlat Oil Field and used for combustion tube experiments presented in our previous work [31]. It should be mentioned that initial rock sample does not contain oil. For combustion tube experiments, the rock sample and oil from Nurlat Oil Field were mixed in a specific ratio. After the combustion tube experiment, the reactor was cooled down for 12 - 15 hours, then the core model was carefully removed from the core holder while maintaining the model structure. The rock samples were collected by vials

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from the zones (T1, T2, T3, T4, T5, T6.1, and T6.2) where thermocouples were installed for further research, as shown in figure 1.

2.2. X-ray phase analysis

The mineralogical composition of rock samples before and after combustion tube experiments was analysed by X-ray diffractometer (XRD). The X-ray phase analysis was performed on a Bruker D2 Phaser diffractometer. Samples were grinded in a mortar with the addition of 5 g of ethanol to get powder samples. The dried sample was loaded on the matte surface of a glass slide, lubricated by vaseline. The surface is pressed and smoothed with a metal plate to get a perfectly flat state. The diffraction patterns of the samples were obtained for the identification of crystalline phases and their percentage in samples.

2.3. Thermogravimetry (TGA) experiments

TGA experiments were performed in the TG 209 F1 Libra therobalance (Netzsch, Germany). A corundum crucible was employed for heating samples inside the therobalance from 30 to 1100 °C under air atmosphere. The heating rate was 10 °C/min was used. The mass of sample was about 100 mg. Before performing experiments, calibration should be carried out. The detailed procedures of experiment and calibration are described by Yuan et al. [7].

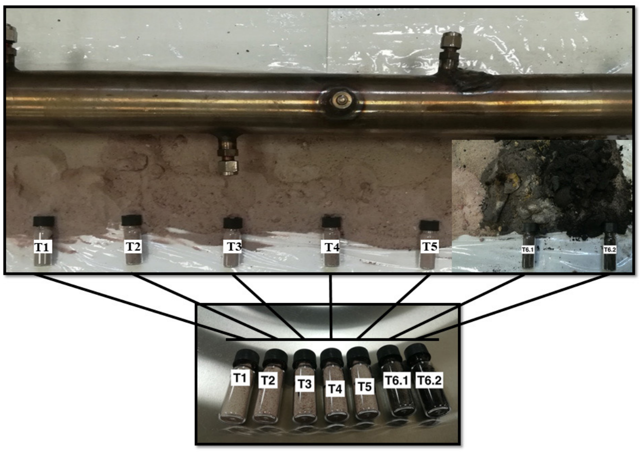

Fig.1. Rock samples obtained after combustion tube experiments

2.5 Thermomagnetic analysis

Thermomagnetic analysis (TMA) is a major method for the diagnosis of ferromagnetic fraction composition in rocks. In this work, TMA analysis was performed to analyses the change of thermomagnetic properties of rock after ISC process. TMA experiments were carried out using a Curie express balance [32]. Temperature dependences of induced magnetization (J_i) up to 800 °C were obtained at a heating rate of 100 °C/min in a constant magnetic field of 0.4 T in the air. Sample mass was about 100 mg. Each sample was heated two-times. The second time heating was performed when the sample cooled down to room temperature after first time heating. The curves of the first and second heating allow evaluating possible mineralogical transformations in the sample.

3. Results and Discussion

3.1 The composition of rock before and after combustion.

XRD spectra of initial oil sample, T3, and T4 are shown in figures 2-4, respectively. Table 2 shows the composition of each sample. The initial rock sample is composed of 96% quartz, 2% kaolinite, and a small amount of albite, calcite, and pyrite. After ISC process of heavy oil, quartz, kaolinite, and albite did not change, but calcite and pyrites disappeared. It means that the calcite was decomposed during combustion process. Simultaneously, it can be concluded that the pyrite (FeS_2) during combustion also was transformed and resulted in the formation of hematite (Fe_2O_3) and anhydrite ($CaSO_4$). The formation of anhydrite resulted from a joint process of calcite decomposition and pyrite transformation. Cementation of sand occurred as a result of the redistribution of the substance of pyrite contractions.

3.2 Organic content of rock before and after combustion.

As shown in figure 1, we can visually observe that the rock was cemented and its color was changed from black (oil-containing rock) to white-gray and reddish-gray. To understand the change of organic content in rock, rock samples were analyzed by TGA. Figure 5 shows the TG-DTG curves of samples T1, T2, T3, T4, T5, T6.1, and T6.2. The organic content, including coke and remaining oil, is shown in table

Table 1

X-ray phase analysis results before and after the ISC-1 experiment

Mineral	Before combustion	After combustion
Quartz (%)	96	96
Kaolinite (%)	2	2
Albite (%)	<1	<1
Calcite (%)	<1	0
Pyrites (%)	<1	0
Hematite (%)	0	<1
Anhydrite (%)	0	<1

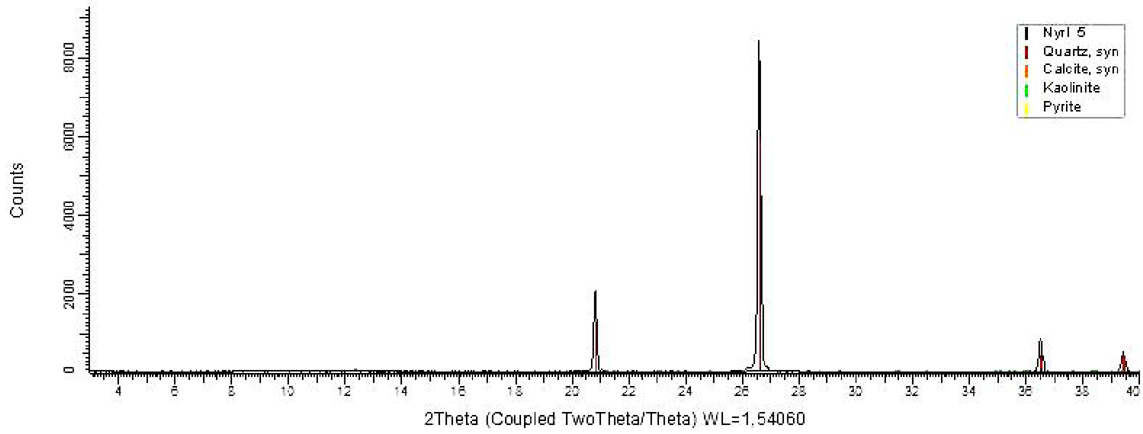

Fig.2. XRD spectrum of initial rock sample before combustion

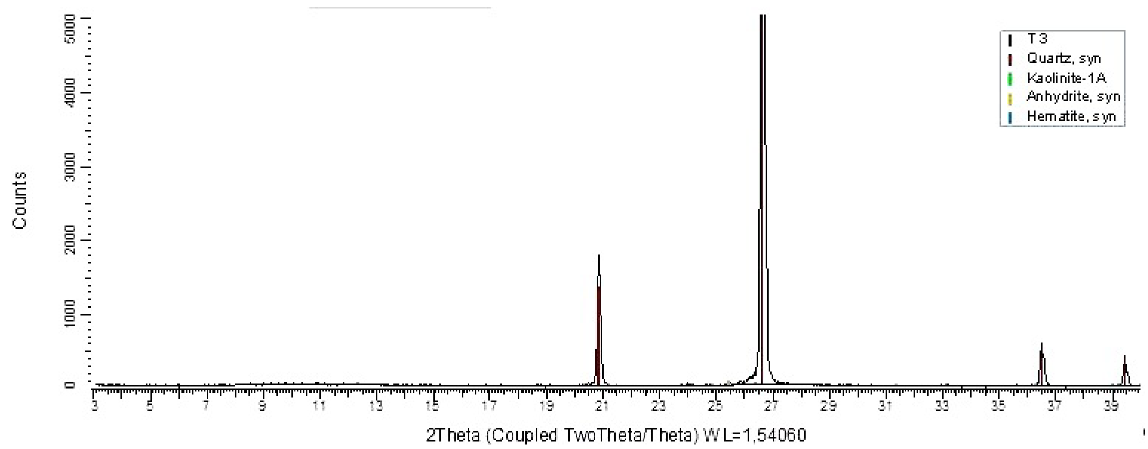

Fig.3. XRD spectrum of rock sample (T3) after combustion

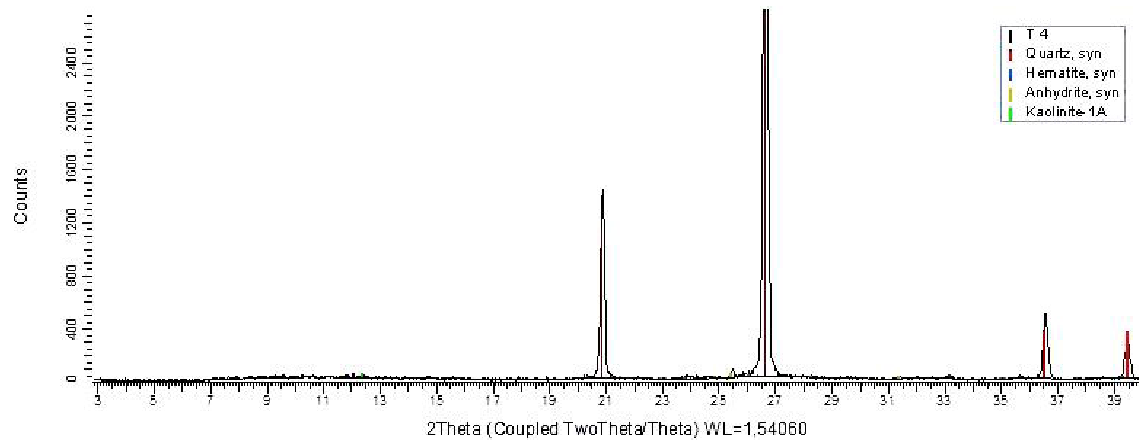

Fig.4. XRD spectrum of rock sample (T4) after combustion

2. Samples T1-T5 contain a very small quantity of organic matters (coke) after combustion, which can be identified from DTG curves where a peak appears at about 550 °C to 730 °C (fig. 5). At < about 500 °C, no mass loss is observed, which means that no remaining liquid organic matters after ISC process. For samples T6.1 and T6.2, mass loss appears at < 500 °C as shown in TG-DTG curves, and sample T6.2 has a much higher mass loss than sample T6.1. These results are in line with that visual observation as shown in figure 1.

3.3 Thermomagnetic change of rock before and after combustion.

There is a significant difference samples among these samples from T1 to T6. Table 3 shows how

Table 2

Organic content of rock samples after combustion

Sample	Coke content (wt.%)	Remaining oil (wt.%)
T1	1.07	≈ 0
T2	0.91	≈ 0
T3	0.87	≈ 0
T4	0.83	≈ 0
Total organic content (wt.%)		
T5	0.86	
T6.1	3.0	
T6.2	8.2	

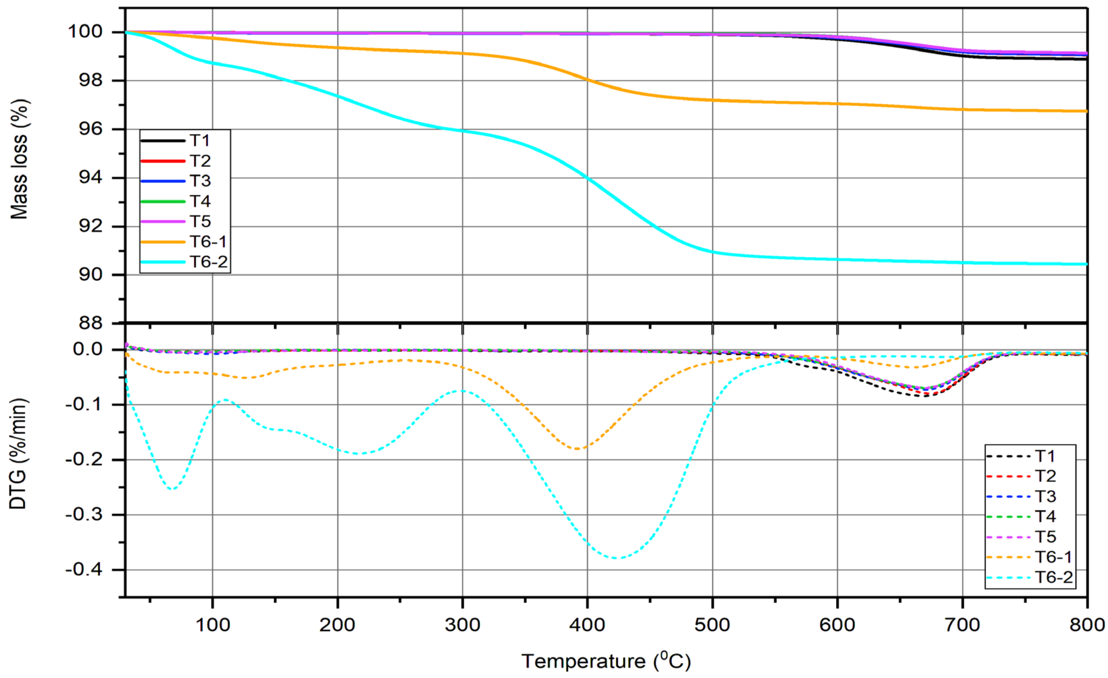

Fig.5. TG/DTG curves of samples T1, T2, T3, T4, T5, T6.1, and T6.2

J_{i2}/J_{i1} ratio is changing from T1 to T6. For sample T1, J_{i2}/J_{i1} ratio is less than 1, which confirms high heating temperatures (above 600 °C) as shown in temperature profile in our previous work [31]). There is no magnetic transformation that can lead to the increase of magnetization during TMA analysis. For samples T1 to T4, J_{i2}/J_{i1} ratio slightly increases, which is a sign that the thermal treatment time of samples under high temperature became less. This is consistent with the process of combustion front propagated from T1 to T6 in ISC process. But in general, J_{i2}/J_{i1} ratio is similar, less than 2. For sample T5, J_{i2}/J_{i1} ratio increases to 6.27 which is much higher than that of samples T1-T4. For sample T6.2, J_{i2}/J_{i1} ratio significantly increases to 30.31. This is because sample T6.2 was not subjected to enough high temperature heating process, and thereby contained more organic (coke + oils), which is proved by TGA analysis. During the TMA experiments, the oils were combusted and new magnetic phases were produced. Simultaneously, we can find that sample T6.2 has a much higher J_{i2}/J_{i1} ratio than initial rock sample, it means that the presence of organic matters (oils) and their combustion can lead the rock minerals from being transformed into magnetic materials.

As can be seen, samples T1 and T2 were mostly transformed under the influence of long-time high temperature caused by combustion process (fig. 6a). Magnetite and hematite are distinguished along the curves, with the Curie temperatures of 580 and 680 °C [33], respectively. During ISC, iron containing minerals were also formed with a Curie temperature of about 320 °C, which were destroyed by further heating

Table 3

Ratio between second and first heating (J_{i2}/J_{i1}) for the sample at room temperature

sample	T1	T2	T3	T4	T5	T6.2	Initial rock sample
J_{i2}/J_{i1}	0.77	1.01	1.39	1.68	6.27	30.31	8.68

process. Most likely, it was magnetic iron sulfide [33]. There was practically no increase in magnetization associated with the formation of new magnetic phases during heating, and all magnetic phases have already formed during ISC experiment. The formation of small amount of magnetite was also observed in the temperature range from 400 to 520 °C. This occurred in a part of the sample that was probably not heated to such temperatures during the ISC. During first heating, the magnetization of the sample dropped by 23% (J_{i2}/J_{i1} = 0.77; see table 3) due to the oxidation of iron sulfide with a Curie temperature of about 320 °C and the oxidation of a part of magnetite (Fe_3O_4) to hematite (Fe_2O_3). Hematite has a spontaneous magnetization more than two orders of magnitude lower than that of magnetite. During the second heating there is no increase in magnetization or the formation of a new magnetic phase (fig. 6b). All organic matters were oxidized and all possible transformations of iron containing minerals at certain oxygen content have already occurred. It should be noted that the increase in magnetization at temperatures of 550-590 °C and 620-650 °C are associated with the thermomagnetic Hopkinson effect [34]. This effect occurs because of the formation in samples of very fine magnetite and hematite with high coercivity [34].

The second type of curves were observed for samples T3 and T4 as shown in figure 7. After the first heating, a slight increase in magnetization was observed, which is associated with the formation of magnetite in the part of the rock that was not heated to temperatures above 400 °C, where organic matter was also preserved. The curves also show the presence of magnetite and hematite.

For sample T5, the increase in magnetization intensity is more significant after the first heating (fig. 6a), which means that new magnetic phases were produced during the heating process. However, as shown in figures 1 and 5, sample T5 contains a similar organic content like samples T1-T4, but an obvious increase in magnetization intensity is observed. We assume that the rock of sample T5 did not undergo enough heating time like sample T1-T4 as it is close to outlet. The experiment was terminated when the combustion front just passed through T6. This leads to those parts of iron-containing minerals were not fully transformed into magnetic phases.

Sample T6.2 has the same characteristics as the initial sample (fig. 6). This indicates that it was not subjected to high temperature heating process like other samples (T1-T5). During the heating process, the minerals was transformed and magnetite was formed with the combustion of organic matters. During the second heating, the magnetization of the sample increases significantly (up to 30 times), and the amount of magnetite also continues to grow. This confirms the aforementioned assumption that rock samples need to undergo enough heating at high temperature to fully complete the transformation of minerals into new magnetic minerals. During the experiment, part of the magnetite turns into hematite during both heating processes.

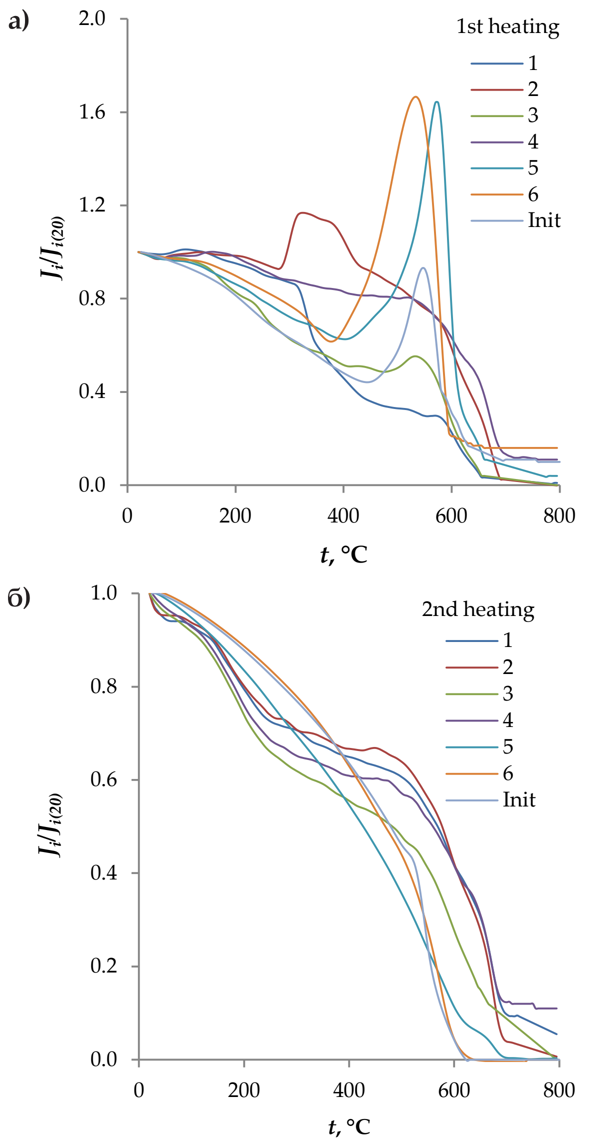

Fig.6. Thermomagnetic curves of samples from zones T1-T6 and initial rock. Each diagram normalized to its magnetization at room temperature. First (a) and second (b) heating

Conclusion

Rock sample obtained after the combustion process can be divided into 3 groups with different magnetic properties. The first group samples (the most heated) that underwent a high-temperature heating with longest time did not show significant changes in thermomagnetic curves, and no increase of magnetization on the second heating curve is observed. The second group samples (the less heated) that show an increase in the induced magnetization above 400 °C, indicating there are still iron-containing minerals that were not fully converted to magnetic phases or presence of organic matter. The third group samples (non-heated) have the highest J_{i2}/J_{i1} ratio, even higher than that of initial rock sample. It can be concluded that the formation of magnetic minerals in rock depends on temperature, heating time, and oil environment. The findings in this work have a great value of developing techniques that can use the magnetic properties change in rock to monitor the location of combustion front, which can provide an indication for the adjustment of ISC process and increase its efficiency.

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Влияние процесса внутрипластового горения на магнитные свойства и состав породы

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Реферат

Внутрипластовое горение (ВПГ) - проверенный, эффективный метод увеличения нефтеотдачи (МУН). В предыдущей работе была изучена возможность применения ВПГ для добычи тяжелой нефти на нурлатском месторождении (НК Татнефть, Россия) с точки зрения извлечения нефти, повышения качества нефти внутри пласта, стабильности фронта горения и т. д. В данной работе было исследовано влияние процесса ВПГ на свойства и состав горных пород. Показано, что в изучаемых горных породах в процессе горения нефти могут образовываться магнитные минералы. Их образование зависит от температуры, времени нагрева и нефтяной среды. По магнитным свойствам образцы разделяются по степени прогревания на более и менее нагретые, и не нагретые с содержанием углеводородов. Изменения магнитных свойств горных пород могут быть использованы для разработки технологий мониторинга фронта горения, что очень ценно для управления процессом ВПГ и его корректировки.

Ключевые слова: магнитные свойства; термомагнитный анализ; методы повышения нефтеотдачи; внутрипластовое горение; горная порода.

Laydaxili yanma prosesinin süxurların maqnit xassələrinə və tərkibinə təsiri

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Xülasə

Laydaxili yanma (LDY) – sınaqdan çıxmiş, effektli neftveriminin artırılması üsuludur (NAÜ). Əvvəllər neftin çıxarılması, lay daxilində neftin keyfiyyətinin yüksəldilməsi, yanma cəbhəsinin sabitliyi nöqteyi-nəzərindən Nurlat yatağında (Tatneft NŞ, Rusiya) ağır neftin hasilatı üçün LDY-nın tətbiqinin mümkünlüyü öyrənilmişdir. Məqalədə LDY prosesinin dağ süxurlarının xassələrinə və tərkibinə təsiri tədqiq edilmişdir. Göstərilmişdir ki, tədqiq olunan dağ süxurlarında neftin yanma prosesi zamanı maqnit mineralları əmələ gələ bilər. Onların əmələ gəlməsi temperaturdan, qızdırılma vaxtından və neft mühitindən asılıdır. Maqnit xassələrinə görə nümunələr qızdırılma dərəcəsinə görə daha çox və daha az qızdırılmış və tərkibində karbohidrogenlər olan qızdırılmamış hissələrə ayrılır. Dağ süxurlarının maqnit xassələrinin dəyişməsi yanma cəbhəsinin monitorinqi texnologiyalarının işlənməsi üçün istifadə edilə bilər ki, bu da LDY prosesinin idarə olunması və ona düzəlişlərin edilməsi üçün olduqca qiymətlidir.

Açar sözlər: : maqnit xassələri; termomaqnit analizi; neftveriminin artırılması üsulları; laydaxili yanma; dağ süxurları.