

EFFECT OF BIOLEACHING ON THE YIELD AND COMPOSITION OF MEIHEKOU OIL SHALE (CHINA)

XUE-QING ZHANG^(a), YU-HONG FEI^(a), YA-SONG LI^(a),
BING ZHOU^(a), HE-JUN REN^{(b)*}, LAN-YING ZHANG^(b)

^(a) Institute of Hydrogeology and Environmental Geology, Chinese Academy of Geological Sciences, Shijiazhuang 050061, China

^(b) Key Laboratory of Groundwater Resources and Environment, Ministry of Education, Jilin University, No. 2519 Jiefang Road, Changchun 130021, China

Abstract. *The paper focuses on investigating the impact of mineral components of Meihekou oil shale on the conversion of organic carbon from the oil shale into shale oil. A number of leaching operations were performed and each product formed in the bioleaching process was analyzed. The analysis showed that the bioleaching technology used is best for oil shale conversion. The yield of shale oil was from 8.3% to 11.2%, and approximately 8.4% of extra shale oil was obtained. During bioleaching a lot of micropores were generated in oil shale, which is favorable to transfer heat from the outside into the inside of the bioleached oil shale sample. Therefore, more shale oil could be obtained through the micropores rapidly, which may avoid shale oil from cracking into shale gas. Finally, bioleaching contributes to the production of more shale oil.*

Keywords: *oil shale, bioleaching, shale oil yield, Thiobacillus ferrooxidans.*

1. Introduction

Oil shale is a kind of sedimentary rock containing organic matter (> 3.5%). The shale oil obtained from oil shale by the retorting technology is an ideal substitute for crude oil. Due to the global energy shortage, it is particularly important to develop and utilize the huge reserves of shale oil as an alternative resource of oil and natural gas.

Oil shale consists of sedimentary inorganic material containing a cross-linked macromolecular organic material called kerogen [1]. The inorganic part mainly consists of quartz, clay, different types of carbonates (CaCO₃, MgCO₃, dolomite), pyrite and Fe₂O₃ [2], as well as trace elements (As, B, Mo, Ni, Zn) [3]. The high sulphur content in oil shale is considered one of

* Corresponding author: e-mail 364471331@qq.com

the biggest challenges in the utilization of oil shale [4], which may cause serious atmospheric pollution.

Studies on the utilization of oil shale have mainly focused on three aspects: combustion for electricity production, retorting for obtaining shale oil and in situ thermal processing [5, 6, 7]. The major component of oil shale is the inorganic mineral, whose heating for shale oil extraction wastes a lot of energy, causing severe environmental pollution [8]. Therefore, oil shale researchers are exploring possibilities to reduce its inorganic mineral content and keep that of kerogen stable, which eventually increases organic content.

At first investigators attempted to remove the inorganic mineral part by using chemical reagents, and some researchers showed that it could be removed from oil shale at a certain concentration of different inorganic acids [9, 10]. However, other scientists reported that kerogen could be attacked by inorganic acids [11, 12], resulting in the decrease of organic content. Moreover, these acids are hazardous and dangerous to human and environment. Therefore, it is highly necessary to work out an economic and environmentally friendly pretreatment process for the extraction of shale oil, during which carbonate and pyrite could be dissolved to increase the relative organic content at mesophilic temperatures, to partially avoid the negative effects arising from retorting and use of inorganic acids.

In the past few years, bioleaching technology using especially *Thiobacillus ferrooxidans* (*T.f.*) has been widely employed in biohydrometallurgy [13]. The bioleaching technology has been used as a pretreatment process to obtain copper, uranium, aurum, and other metals [14, 15]. At first, the bioleaching technology applied to oil shale was only designed to remove carbonate [16, 17]. However, recent researches show that *T.f.* can be used to enrich organic matter and keep it stable [18, 19], and also to remove sulfur from oil shale [20, 21, 22].

Shale oil is the most valuable product of oil shale. At the same time, there are only few studies on the relationship between bioleaching and shale oil yield from retorting. This paper mainly focuses on the changes of the microstructure and components of oil shale, and the increased shale oil yield favoured by bioleaching.

2. Materials and methods

2.1. Materials

The oil shale used in bioleaching experiments was taken from Meihekou City in Jilin Province, China. The oil shale sample was crushed to particles 1–2 mm in diameter. Table 1 shows the data on proximate, ultimate and Fischer assay analyses of Meihekou oil shale sample.

Table 1. Dry basis analyses of Meihokou oil shale sample

Proximate analysis, wt%, ad		Elemental analysis, wt%, ad		Fischer assay analysis, wt%	
Moisture	2.78	C	59.87	Shale oil	8.3
Ash	72.51	H	7.45	Gas	5.2
Volatile matter	22.24	N	1.01	Water	5.1
Fixed carbon	2.47	S	1.73	Semicoke	81.4

2.2. Bacteria and medium

The medium used for bioleaching was a modified 9K medium (M9K): 3.0 g/L $(\text{NH}_4)_2\text{SO}_4$, 0.1 g/L K_2HPO_4 , 0.5 g/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.1 g/L KCl, 0.013 g/L $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 1.0 g/L sulfur, adjusted to pH 2 with H_2SO_4 . The bacteria, which are chemolithotrophic, obtain their energy from the oxidation of pyrite and added sulfur.

The bacterial strain was isolated from the acid mine drainage (AMD) in a dump leaching plant (Dexing Copper Mine, China). The screening and purification of the bacterium were conducted using a 9K medium according to the dilution-plate methods. The colonies were picked on the 10^{-6} dilution plate and grown in the 50 ml same liquid medium. After being shaken for 7 days, all cultures were sterilized at 4 °C with shaking to stop the microbial metabolism, and the cultures were further filtered to separate mineral powder residues and the cells. The pH of the filtered culture solutions was determined. At last, a bacterium was selected, and identified to be *T. ferrooxidans* by 16S rDNA sequence analysis and the Biolog bacterial identification system (Biolog, USA). The bacterium was deposited in China General Microbiological Culture Collection Center (CGMCC) under CGMCC Accession No. 6541.

2.3. Leaching experiments

All experiments were performed in 250 mL Erlenmeyer flasks at 30 °C and 150 rpm agitation under aseptic conditions. 10 g of oil shale sample was added to 100 ml M9K in each Erlenmeyer flask, the whole bioleaching process lasted for 15 days. Three kinds of samples were prepared:

Sample A: the oil shale powder was sterilized in closed vessels by dry heat at 80 °C for 100 h to avoid the growth of indigenous microorganisms.

Sample B: take a portion of Sample A leached for 16 days in the modified 9K medium, under aseptic conditions.

Sample C: take a portion of Sample A bioleached for 16 days in the modified 9K medium with *T. ferrooxidans*.

The bioleaching experiments were carried out in two stages. The first stage involved the growing of *T. ferrooxidans* in M9K for three days (only M9K without *T. ferrooxidans* as parallel control). The second stage consisted in that 10 g of Sample A was added and a final 10% (100 g/L) ore

slurry was prepared. By carrying out the batch experiments, samples were prepared 500 g each.

2.4. Sample analysis

During the bioleaching experiments, free bacteria in solution were counted by direct counting, using a Thoma chamber with an optical microscope (1000×), the soluble Fe^{3+} concentration in the bioleaching solutions was determined by spectroscopy, the pH was monitored at room temperature with a Mettler DELTA 320 pH meter (USA).

To explore the changes of the microstructure and components of oil shale, samples A, B and C were air dried and analyzed by scanning electron microscopy (SEM; Hitachi S-4800, Japan), infrared spectral analysis (IR; WQF-520, China), X-ray diffractometry (XRD; Shimadzu XRD-7000S/L, Japan) and X-ray fluorescence (XRF; Shimadzu MXF-2400, Japan). For all experiments, chemical grade reagents and distilled water were used.

Shale oil yield was determined by Fischer assay analysis according to ISO 647-74. Approximately 50 g of each sample was heated in an aluminum retort to 520 °C at a heating rate of 12 °C/min. The oil yield was calculated as percentage based on the original mass and the gas loss (non-condensable) was calculated as the difference between the initial mass and the sum of masses of oil, water and ash.

3. Results and discussion

3.1. Bioleaching process analysis

Figure 1 illustrates different changes taking place during the bioleaching process. At the first stage, the pH kept stable, no Fe^{3+} was detectable, only *T. ferrooxidans* grew to about $1.5 \times 10^7/\text{mL}$. At the second stage, when Sample A was added, the pH increased to 4 immediately, *T. ferrooxidans* appeared during an adjustment period within two days, then appeared in the exponential phase, large amounts of bacteria were reproduced in the liquor of Sample C, no bacteria were found in the liquor of Sample B. In the liquor of Sample B, the pH kept at 4, the concentration of Fe^{3+} increased to 2 g/L and then kept stable. In the liquor of Sample C, the pH decreased to 2.3 and kept stable on the twelfth day, the Fe^{3+} concentration increased to 8 g/L and kept stable on the twelfth day. Significant changes in the weight of the two samples were observed, the weight of Sample B and Sample C decreased to 9.3 g and 8.33 g, respectively.

These results show that the liquors of Sample B and Sample C differ significantly in microbial metabolism, while pyrite and added sulfur can support the growth of *T. ferrooxidans*.

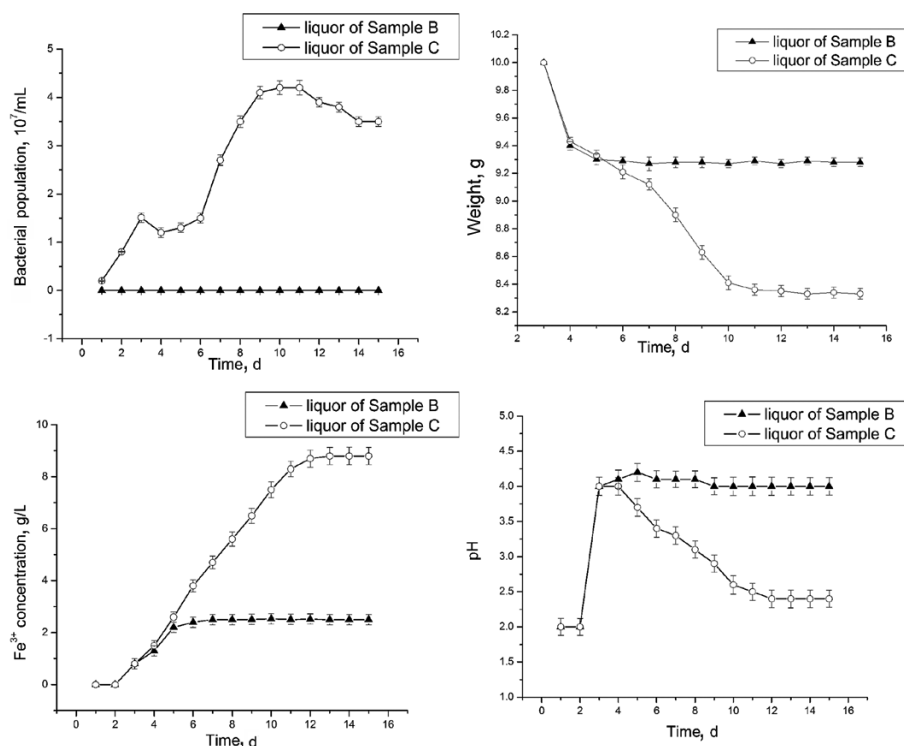


Fig. 1. Changes in pH, bacterial population, Fe^{3+} concentration and sample weight during bioleaching.

3.2. Changes in the texture of different oil shale samples

SEM is intensively used to observe the morphological features of mineral surfaces of different samples, to reveal the texture changes of mineral samples. The typical features of oil shale samples revealed by SEM are shown in Figure 2.

A comparison of SEM images of untreated and treated oil shale samples shows their surfaces to significantly differ. It can be clearly seen from SEM images that the oil shale sample surface is relatively smooth before leaching (Fig. 2a), while many minute cracks were observed in the matrix of Sample B (Fig. 2b) as more inorganic mineral was dissolved during the bioleaching process. A rough, uneven and porous structure was formed in the matrix of Sample C (Fig. 2c), and numerous bacteria were observed on its surface, in the direction of the black arrow (Fig. 2d). It indicates that more inorganic mineral matter was dissolved by bioleaching than was leached by M9K. The microporous structure formed in the matrix of Sample C contributes to the release of shale oil.

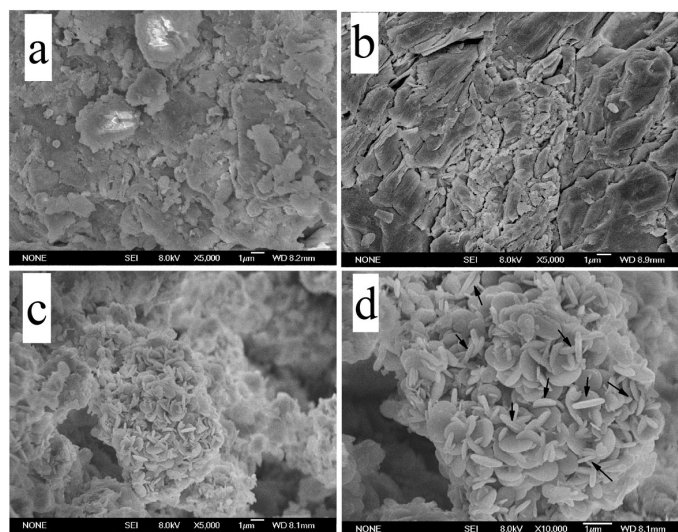


Fig. 2. The microstructures of different oil shale samples examined by SEM: a: Sample A; b: sample B; c: Sample C; d: the target area at a high magnification of Sample C.

3.3. Changes in the inorganic component of different oil shale samples

Approximately 2 g of each oil shale sample was placed in a sample holder (diameter 25 mm) and analyzed in a Shimadzu MXF-2400 diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with electrical parameters of 40 kV and 40 mA. The scanning angles ranged from 3 to $70^\circ(2\theta)$ (speed of 2°min^{-1}).

X-ray diffractograms depicting changes of different oil shale samples are presented in Figure 3. The XRD spectra show the presence of illite,

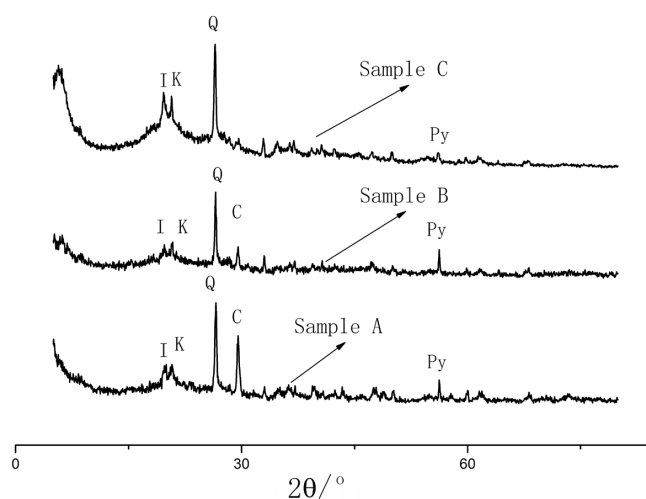


Fig. 3. XRD patterns of different oil shale samples (I – illite, K – kaolinite, Q – quartz, C – calcite, Py – pyrite).

kaolinite, quartz, calcite and pyrite in Sample A. The XRD for Sample B shows that the peak of calcite is significantly decreased, which is due to the acid leaching by M9K. The XRD for Sample C shows that the peak of calcite has almost disappeared and the peak of pyrite is significantly decreased. The authors conclude that *T. ferrooxidans* oxidized pyrite and the added S to get energy for reproduction, and more H^+ was produced to dissolve carbonate further.

Table 2 presents the results of XRF analyses of oil shale samples, which show that the relative content of Fe_2O_3 and SO_3 was significantly reduced. Considering that bioleaching decreased the weight of oil shale samples about 19.7%, the rate of removal of CaO, FeO and SO_3 was calculated, by means of Equation (1), to be respectively 96.6%, 77.4% and 95.4%:

$$H = \frac{W_1 \times O_1 - W_2 \times O_2}{W_1 \times O_1}, \quad (1)$$

where H is the removal rate; W_1 is the mass of oil shale sample before bioleaching; W_2 is the mass of oil shale sample after bioleaching; O_1 is the component content before bioleaching; O_2 is the component content after bioleaching.

Table 2. XRF analysis of different oil shale samples, wt%

Component	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	MnO	SO ₃
Sample A	51.1	10.3	7.1	9.63	1.17	0.56	1.14	0.82	0.2	0.19	1.57
Sample B	55.3	11.2	3.93	9.72	1.21	0.59	1.17	0.89	0.22	0.23	1.61
Sample C	61.7	14.81	0.3	2.71	1.28	0.63	1.05	0.93	0.21	0.36	0.09

3.4. IR analysis of oil shale samples

Oil shale samples weighing 0.5 mg were hand ground to fine powder. Each sample was mixed with 200 mg of dry KBr powder, uniformly mixed and then reground. The entire sample was transferred to a die and pressed under vacuum in a standard way. The spectra were recorded between 4000 cm^{-1} and 400 cm^{-1} .

To compare the functional group changes in different oil shale samples, the components of the samples were examined by IR analysis. Figure 4 presents the spectral patterns of oil shale samples. As shown in the figure, the main functional groups C–H (2925 cm^{-1} , 2850 cm^{-1}), C=C (1600 cm^{-1}) and Si–O–Si (1060 cm^{-1}) underwent significant changes during bioleaching. The spectral intensity of Si–O–Si increased after bioleaching, which supports the findings of XRD. The peak of C–H and C=C gradually strengthened in Sample B and Sample C. These results indicate that the organic matter kept stable and its relative content increased during the bioleaching process.

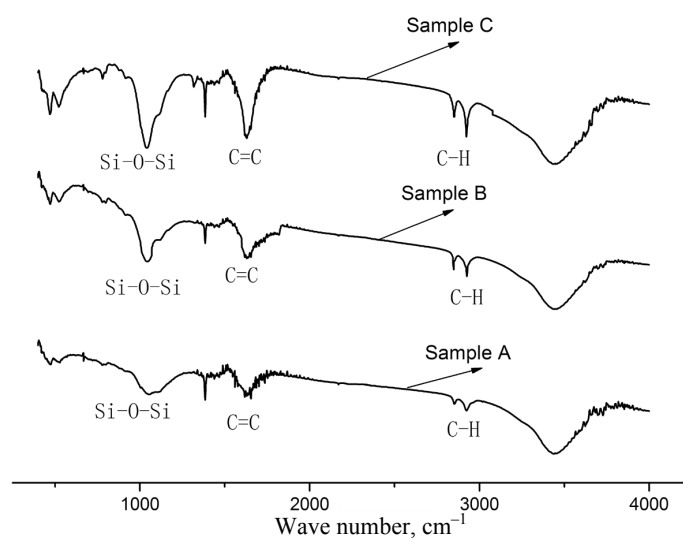


Fig. 4. IR spectral analysis of different oil shale samples.

3.5. Changes in shale oil yield of different oil shale samples

As seen from Figure 5, the shale oil yield increased from 8.3% before bioleaching to 11.2% after bioleaching, that of semicoke decreased respectively from 81.4% to 77.8% and gas loss from 5.2% to 4.8%. Decrease in the gas loss proves that less shale oil would be cracked into shale gas after bioleaching, which enables more shale oil to be obtained. The authors found

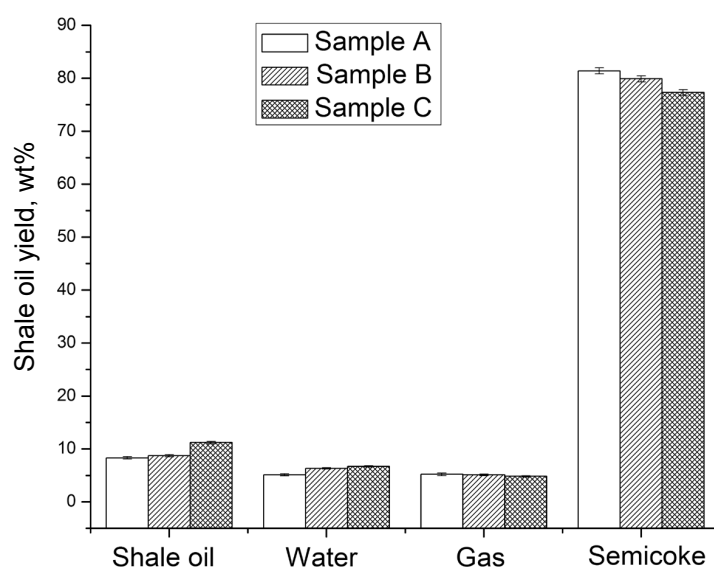


Fig. 5. Fischer assay analysis of oil shale samples.

using Equation (2) that approximately 8.4% of extra shale oil was obtained after bioleaching:

$$S = \frac{W_2 \times Q_2 - W_1 \times Q_1}{W_1 \times Q_1}, \quad (2)$$

where S is the increased shale oil content; W_1 is the mass of oil shale sample before bioleaching; W_2 is the mass of oil shale sample after bioleaching; Q_1 is the shale oil yield before bioleaching; Q_2 is the shale oil yield after bioleaching.

The increment in shale oil yield should be correlated with the demineralization by $T.f.$ Due to the demineralization, more organic matter was exposed, the organic matter could be heated evenly, quickly, more shale oil could pass the microporous fleetly oil shale during the dry distillation process, which prevents shale oil from cracking into shale gas, and, finally, more shale oil could be obtained. The bioleaching process is very inexpensive to carry out, is economically beneficial and environmentally friendly.

4. Conclusions

The bacteria obtained from AMD of Dexing Copper Mine in China showed good performance in the bioleaching of oil shale. The results of the leached residues analysis indicate that the composition and structure of bioleached minerals have changed during the bioleaching process. Carbonate is leached first at low pH, then the added sulfur and pyrite in the oil shale are oxidized to produce H^+ , the H^+ can corrode the carbonate further. Finally, a microporous structure in the matrix of bioleached residues was formed. The removal of the mineral matrix is favorable to transfer heat from the outside towards the inside of the bioleached oil shale sample. Therefore, more shale oil could be obtained through the micropores rapidly, which may avoid shale oil from cracking into shale gas. Finally, more shale oil can be produced after bioleaching.

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