

Oil Shale

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2026 v.43 N.4



International open access scientific journal
of the Estonian Academy of Sciences
published in collaboration with
Tallinn University of Technology
and the Geological Survey of Estonia

Published since 1984

OIL SHALE 2026, Vol. 43, No. 4

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Abstracted/indexed in Science Citation Index Expanded (Web of Science),
Current Contents – Engineering, Computing & Technology (Web of Science),
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The journal is published quarterly

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Printed by Alfapress OÜ, Reti tee 8, 75312 Peetri, Estonia

Rapid-heating open-system thermal simulation of oil shale residue and hydrocarbon product evolution characteristics

Zhisheng Luan^(a), Li Li^(a), Wujiang Kang^(a), Pengfei Cheng^(a), Zhifa Ni^(a), Xingwen Zhang^(a), Zhiqiang Yang^(a), Ailin Jiang^(a), Pingchang Sun^{(b)*}

^(a) Exploration & Development Research Institute of Liaohe Oilfield Company, PetroChina, Panjin, Liaoning 124010, China

^(b) College of Earth Sciences, Jilin University, Changchun, Jilin 130061, China

Received 6 November 2025, accepted 21 October 2026, available online 23 October 2026

Abstract. In recent years, in-situ conversion has shown great potential for large-scale oil shale exploitation, but the evolution of hydrocarbon products and residues during thermal conversion remains insufficiently studied. Using oil shale samples from the Fushun, Huadian, and Meihe basins, we conducted heating experiments in a rapid open system to investigate hydrocarbon generation and residue evolution at different stages, providing theoretical support for in-situ recovery. At ≤ 300 °C, water accounts for 40.0–57.4 wt.%, oil yield is below 1 wt.%, and hydrocarbon potential remains excellent. At 400–475 °C, organic matter is greatly consumed, with TOC reduced by 7.7–9.8 wt.%, and S_2 conversion reaches 96.19–97.18%. Hydrocarbon potential drops from excellent to good, marking the main oil generation and expulsion stage. At 520 °C, oil and water yields stabilize, gas yield rises slightly with dry gas as the main component, and residual potential gradually declines. Fushun oil shale is dominated by type I kerogen, whereas Huadian and Meihe oil shales are dominated by type II, with decreasing oil-generating capacity. Organic matter enters the oil window at 300 °C and peaks at 475 °C. We recommend 400–475 °C as the optimal heating range for oil shale in-situ conversion.

Keywords: oil shale, thermal simulation, oil and gas products, organic matter expulsion, in-situ conversion.

1. Introduction

Oil shale is an important unconventional energy source, with an estimated in-situ resource of 411×10^9 tons [1–4]. Due to its abundant resources and the feasibility of development and utilization, it is listed as a very important substitute energy source for the 21st century, similar to oil, natural gas, and

* Corresponding author, 1015287387@qq.com

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coal, all of which are non-renewable fossil fuels. Oil shale has developed during multiple geological historical periods, with a wide distribution range; therefore, the research and exploration of oil shale are of great significance in many countries [5–7]. In-situ mining can be analogous to the in-situ rapid hydrocarbon generation process [8–10], which is an effective way to carry out large-scale clean utilization of oil shale. Multiple pilot tests on the in-situ conversion of oil shale have been conducted domestically and internationally. The in-situ conversion technology developed by Zhongcheng Group features a heating temperature of approximately 520–550 °C, achieving a high oil shale yield after ten days of continuous heating. The in-situ conversion technology developed by Jilin University adopts a heating temperature above 400 °C, realizing gas and oil production after 15 and 17 days of heating, respectively [11, 12].

The hydrocarbon generation process in sedimentary basins can be considered a chemical reaction process under thermodynamic conditions (macromolecules decompose into small molecules), and its chemical kinetic equation can be used for quantitative and dynamic description [13]. In the laboratory, it is possible to simulate the maturity of organic matter under different heating rates under controlled temperature and time [14]. In the past decade, in order to explore the thermal evolution process and hydrocarbon generation mechanism of organic matter, a large number of thermal simulation experiments have been conducted on organic matter, such as the simulation of hydrocarbon generation under different conditions, the composition and evolution characteristics of gaseous and liquid products, the relationship between hydrocarbon yield and maturity, and the hydrocarbon generation potential of kerogen and source rocks [15–21]. These studies indicate that heating plays an important role in the in-situ conversion process of oil shale. Furthermore, the organic matter expulsion and changes in residual components during the heating process have not been systematically studied. This study aims to conduct a staged heating of oil shale in an open system, studying the changes in hydrocarbon products and residual products at each heating stage, in order to provide laboratory data to support the optimization of in-situ conversion temperatures for oil shale [22–25].

2. Materials and methods

A total of three typical oil shale samples were selected for testing and analysis in this study, including one from the Fushun Basin (FS), one from the Meihe Basin (MH), and one from the Huadian Basin (HD) (Fig. 1). Open-system thermal simulation experiments, industrial analysis, total organic carbon (TOC) analysis, and rock pyrolysis analysis were conducted in the Key Laboratory of Oil Shale and Associated Minerals in Jilin Province. The open-system thermal simulation experiment facilitates obtaining the products at

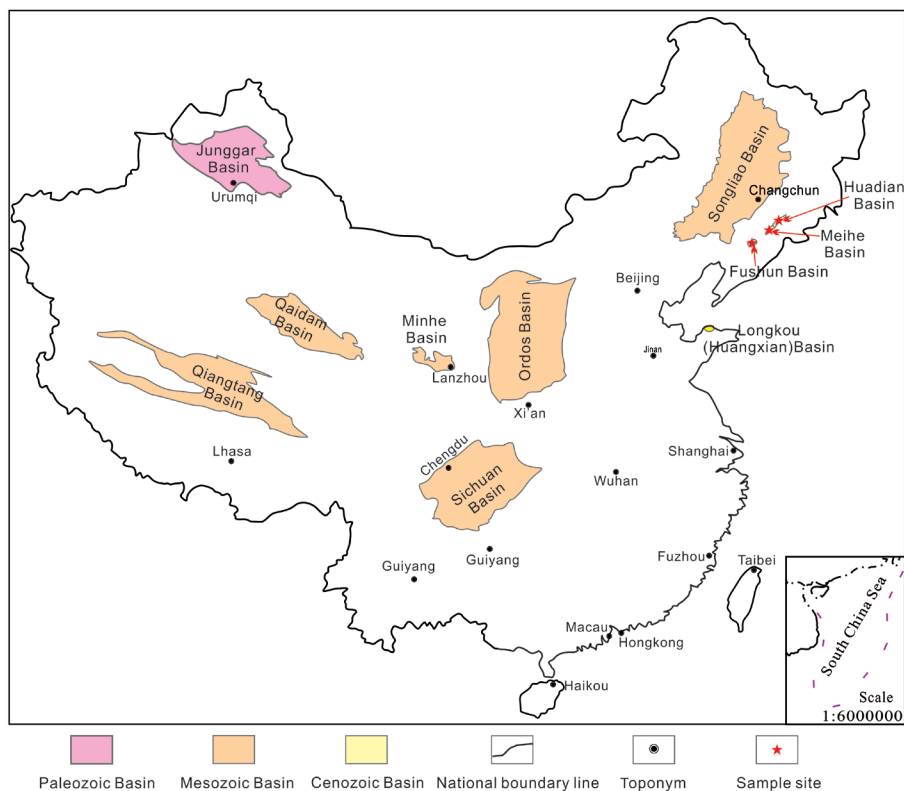


Fig. 1. Sample locations and distribution of oil shale basins in China.

each heating stage and effectively avoids the impact of secondary cracking on the identification of products at different heating stages.

Approximately 300 g of each sample (particle size < 3 mm) was evenly divided into six equal parts (attempting to maintain homogeneity among the samples) and heated in a dry open system according to the standard SH/T0508-92 of the China Petroleum and Chemical Industry in a low-temperature pyrolysis furnace. The heating procedure consisted of six stages. In Stage I, the sample in the first aluminum retort was heated to 185 °C and kept at a constant temperature for 30 min. In Stage II, the sample in the second aluminum retort was heated to 300 °C and maintained at this temperature for 30 min. In Stages III and IV, the samples in the third and fourth aluminum retorts were heated to 400 °C and 475 °C, respectively, and each was kept at a constant temperature for 30 min. In Stage V, the sample in the fifth aluminum retort was heated to 520 °C after which heating was stopped. In Stage VI, the sample in the sixth aluminum retort was heated from room temperature to 520 °C and then maintained at 520 °C for 30 min.

The heating rate for each set of experiments was maintained at 5 °C/min. After the experiment, the mass of the liquid products from the thermal

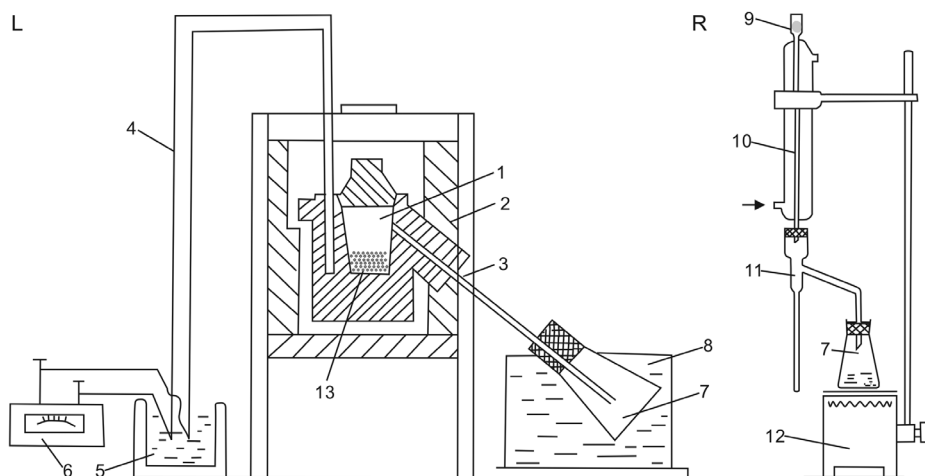


Fig. 2. Open-system thermal simulation device and oil–water separation device [14]: 1 – aluminum drum, 2 – heating furnace, 3 – outlet pipe, 4 – thermocouple, 5 – cold-end constant-temperature regulator, 6 – electrical cabinet, 7 – receiver, 8 – cooling drum, 9 – absorbent cotton, 10 – condenser tube, 11 – constant water supply pipe, 12 – heating platform, 13 – sample. Abbreviations: L – heat simulation device, R – oil–water separation measurement device.

simulation (i.e., shale oil and water) was weighed. The mass of the water was obtained using the solvent extraction method, thereby determining the mass of the shale oil. The heated samples were referred to as residues, and their mass was directly measured after cooling. The weight difference between the total sample mass and the mass of the liquid products plus residues was attributed to gas products (including a small amount of lost components).

The calorific value test was conducted using the standard method for coal calorific value determination, namely “Determination of Calorific Value of Coal” (GB/T213-2003). This experiment used an SDC311/5015 type calorimeter produced by Sandao Company, with a temperature measurement range of 5–44 °C and an instrument resolution of 0.0001 °C, with an error of < 0.15%. The ash content test was carried out by heating the samples to 850 °C in a muffle furnace, and the calculation was based on the change in sample mass before and after heating [26]. According to the standard GB/T 19145-2003, the organic carbon content was determined using a Leco-CS230 carbon-sulfur analyzer. According to the standard GB/T 18602-2012 [27], a Rock-Eval VI pyrolyzer was used to test the pyrolysis parameters of the residues at each heating stage of the three samples. The hydrogen index (HI) ($S_2/\text{TOC} \times 100$) and oxygen index (OI) ($S_3/\text{TOC} \times 100$) values were calculated using the TOC content and pyrolysis parameters.

3. Results

3.1. Characteristics of product content changes at different heating stages

According to the different heating temperature intervals, the characteristics of product content after thermal simulation of the three samples are shown in Table 1. The results indicated that the cumulative content changes of thermal simulation products at different heating stages for different samples generally showed a similar trend (Fig. 3).

Table 1. Thermal simulation products of oil shale

Basin	Sample	Oil yield, wt%						Water yield, wt%					
		I	II	III	IV	V	VI	I	II	III	IV	V	VI
Fushun Basin	FS	0.2	0.5	5.0	13.3	15.2	15.5	1.0	1.4	2.0	2.5	3.3	3.5
Meihe Basin	MH	0.2	0.8	3.0	7.4	8.3	8.6	3.0	3.5	4.0	4.9	6.0	6.1
Huadian Basin	HD	0.4	0.9	3.7	8.7	8.8	9.0	2.5	3.0	4.3	5.8	6.6	6.8
Basin	Sample	Gas and loss, wt%						Semi-coke yield, wt%					
		I	II	III	IV	V	VI	I	II	III	IV	V	VI
Fushun Basin	FS	2.4	2.4	2.5	3.0	3.0	3.2	96.4	95.7	90.5	81.2	78.5	77.8
Meihe Basin	MH	0.7	1.5	4.0	4.6	4.7	4.9	96.1	94.2	89.0	83.1	81.0	80.4
Huadian Basin	HD	1.1	2.1	3.6	3.7	3.8	4.2	96.0	94.0	88.4	81.8	80.8	80.0

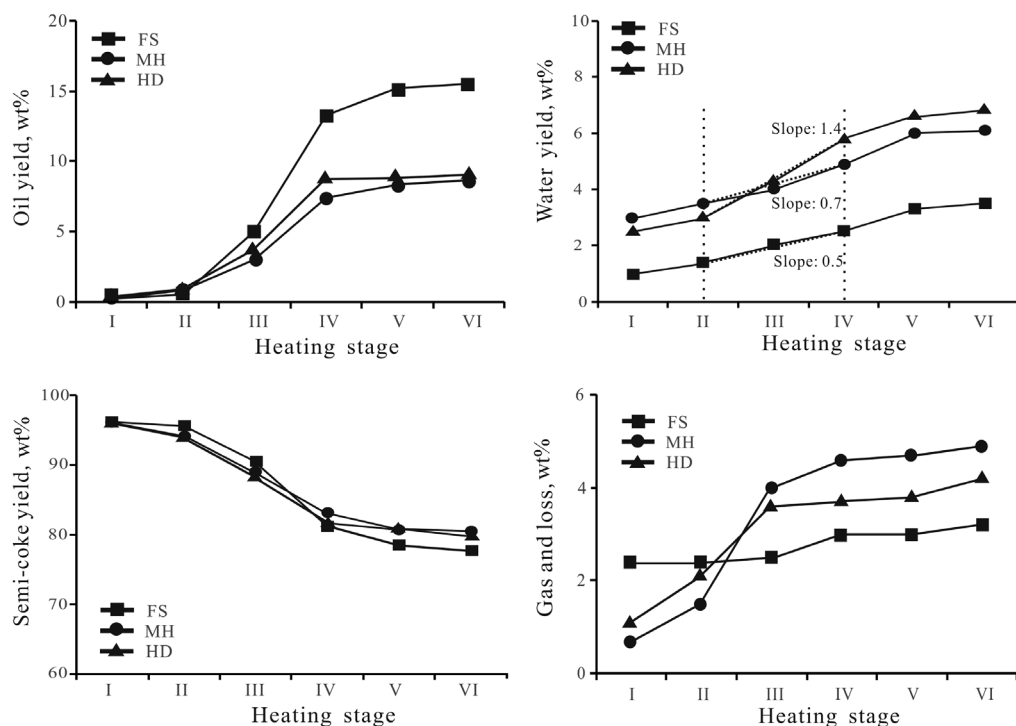


Fig. 3. Percentage content of cumulative component changes at each heating stage.

3.1.1. Oil yield change

With the increase of thermal simulation temperature, the overall oil yield of oil shale gradually increased. The oil yield in Stages I–II was very low, and the oil yields of the three samples were all < 1 wt%. In Stages III–V, the oil yield increased significantly. Among the samples, the oil yield of the FS sample increased the most, reaching 10.2 wt%, while the oil yields of the MH and HD samples increased by 5.3 wt% and 5.1 wt%, respectively. This stage corresponded to the extensive cracking of organic matter to generate oil, indicating that this temperature interval was the main oil-generation window. By Stage VI, the oil yield showed almost no change or a slight increase.

3.1.2. Water yield change

With increasing heating temperature, the water yield showed a slow increasing trend. The characteristics of water yield change for the three samples were similar. The FS, MH, and HD samples had already discharged a large amount of water in Stages I–II, with water discharge ratios of 40.0 wt%, 57.4 wt%, and 44.1 wt%, respectively, indicating that low-temperature heating mainly released water. During Stages III–IV, water was produced along with the

pyrolysis of organic matter. Among these samples, HD had the highest water yield, reaching 1.5 wt%, followed by MH and FS with water yields of 0.9 wt% and 0.5 wt%, respectively. Finally, almost all the water in the three samples was discharged by Stage V.

3.1.3. Residue yield change

The residue yield generally decreased with increasing heating temperature. The residue yields of the FS, MH, and HD samples decreased most rapidly in Stages III–IV, with changes of up to 9.3 wt%, 6.9 wt%, and 6.6 wt%, respectively.

3.1.4. Gas yield change

The gas yield generally increased with increasing heating temperature. In Stages I–II, the gas yield changed slowly. The gas yields of the MH and HD samples increased significantly in Stage III, reaching 4.0 wt% and 3.6 wt%, respectively. In Stages IV–VI, the cumulative gas yields of the FS, MH, and HD oil shale samples increased slightly.

3.2. Organic matter geochemical characteristics at each heating stage

3.2.1. TOC

The higher the TOC content, the greater the organic matter abundance. The TOC test results for the three oil shale samples and the residues after the heating stages are shown in Table 2 and Figure 4. The trend of the TOC data was roughly similar at each heating stage. The TOC of the original FS, MH, and HD oil shale samples was 23.1 wt%, 23.8 wt%, and 25.7 wt%, respectively. The TOC of the three groups of samples did not show significant changes in Stages I–II and V–VI, but it decreased significantly in Stages III–IV. The MH sample decreased the most at these stages, with a reduction of up to 9.8 wt%, followed by the FS oil shale with a reduction of 9.2 wt% and the HD oil shale with a reduction of 7.7 wt%.

Table 2. Characteristics of organic carbon content changes in oil shale at different heating stages, wt%

Basin	Sample	Original sample	Heating stage					
			I	II	III	IV	V	VI
Fushun Basin	FS	23.1	22.3	21.5	19.4	10.2	9.9	9.6
Meihe Basin	MH	23.8	23.5	23.0	20.9	11.1	10.5	9.9
Huadian Basin	HD	25.7	25.1	25.1	23.8	16.1	14.6	14.5

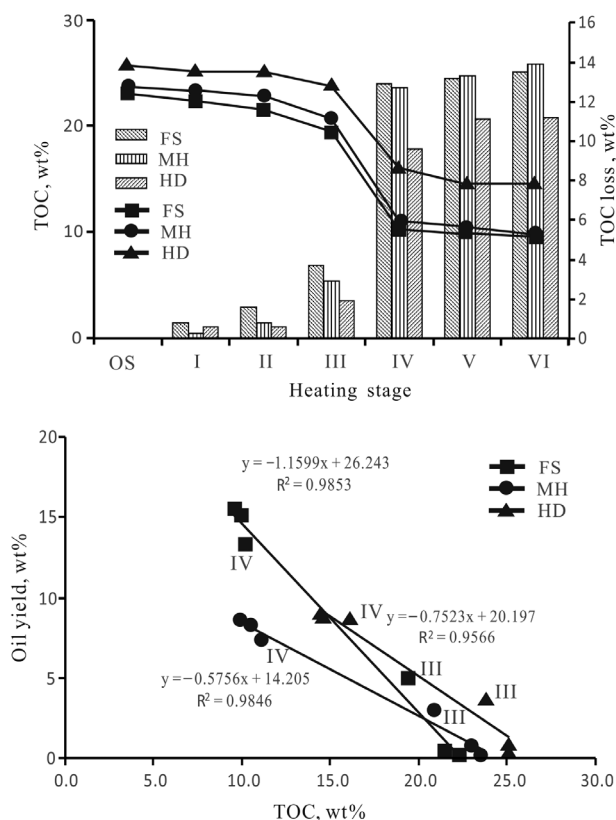


Fig. 4. Organic carbon content of oil shale residues at different heating stages.

A significant negative correlation was observed between the TOC content and oil yield of the three sample groups, with all correlation coefficients (R^2) > 0.95 . During Stages III–IV (400–475 °C), TOC dropped sharply and oil yield increased steeply synchronously; these stages contributed 86–96.7% of the total oil yield, directly confirming that this temperature interval represented the critical stage for large-scale organic matter decomposition and concentrated hydrocarbon generation. When the temperature exceeded 475 °C, the changing trend slowed and oil production efficiency decreased remarkably, which verified that this interval could achieve maximum oil yield with minimal organic matter consumption, thus providing a basis for temperature setting in engineering applications.

The slope of the TOC–oil yield curve of FS oil shale was significantly higher than that of the MH and HD samples, indicating that FS oil shale had a higher conversion efficiency of organic matter to oil. This quantitative difference also provided direct data support for the differentiated design of temperature parameters in the in-situ exploitation of different types of oil shale.

3.2.2. Pyrolysis of rocks

The pyrolysis parameters S_1 and S_2 of the residues at various heating stages were analyzed to understand the characteristics of free hydrocarbons and pyrolytic hydrocarbons of the organic matter in the residues at each heating stage of the oil shale (Table 3).

Table 3. Organic geochemical parameters of oil shale samples at different heating stages

Sample		$T_{\max}$, °C	S_1 , mg/g	S_2 , mg/g	PI	S_3 , mg/g	T OC	HI	OI	$S_1 + S_2$	Organic matter type
FS	OS	430	1.18	176.88	0.01	0.84	23.10	735	3	178.10	I
	I	437	2.61	169.41	0.02	0.83	22.30	760	4	172.00	
	II	447	3.74	162.51	0.02	0.64	21.50	758	3	166.30	
	III	450	7.73	105.60	0.07	0.46	19.40	546	2	113.30	
	IV	455	0.97	4.98	0.16	1.48	10.20	49	15	6.00	
	V	540	0.75	4.00	0.16	2.30	9.90	40	23	4.80	
	VI	556	0.29	1.40	0.17	2.33	9.60	15	24	1.70	
MH	OS	427	1.24	110.93	0.02	1.93	23.80	579	14	112.17	II
	I	436	0.89	105.11	0.01	1.79	23.50	445	13	106.00	
	II	445	2.57	95.24	0.04	1.75	23.00	502	13	97.81	
	III	448	2.95	66.67	0.08	0.91	20.90	300	8	69.62	
	IV	459	1.03	4.23	0.20	1.59	11.10	42	16	5.26	
	V	543	1.41	3.89	0.27	1.47	10.50	41	15	5.30	
	VI	559	0.65	0.89	0.42	1.54	9.90	10	17	1.54	
HD	OS	431	1.79	114.42	0.02	20.66	25.70	391	80	116.21	II
	I	439	2.87	109.07	0.02	19.92	25.10	457	79	111.94	
	II	446	2.33	100.92	0.02	6.09	25.10	438	24	103.25	
	III	449	3.63	79.83	0.04	2.61	23.80	336	11	83.46	
	IV	459	2.21	4.21	0.34	2.73	16.10	24	16	6.42	
	V	540	0.95	1.80	0.34	2.41	14.60	11	14	2.75	
	VI	656	0.89	1.35	0.40	2.70	14.50	8	16	2.24	

S_1 generally represents free hydrocarbons that have been generated but remain trapped in the pores of the sample rock and have not been expelled [28]. The S_1 values of the three original samples (FS, MH, and HD) were relatively small, at 1.18 mg/g, 1.24 mg/g, and 1.79 mg/g, respectively. During Stages I–III, the S_1 values of the three groups of samples increased rapidly and reached their maximum values, with the highest S_1 contents of the FS, MH, and HD samples being 7.73 mg/g, 2.95 mg/g, and 3.63 mg/g, respectively. As heating continued, the free hydrocarbons were expelled, and the S_1 values returned to low values.

S_2 represents pyrolytic hydrocarbons generated by the pyrolysis of organic matter, i.e., organic matter in the rock that can generate hydrocarbons but has not yet done so, reflecting the potential hydrocarbon generation capacity of the sample [29]. The pyrolytic hydrocarbon content (S_2) of the three oil shale samples showed a significant decreasing trend with increasing temperature (Table 3). The S_2 values of the three original samples (FS, MH, and HD) were 176.88 mg/g, 110.93 mg/g, and 114.42 mg/g, respectively. During Stages I–II, the S_2 values of the three groups of samples changed little, indicating that limited pyrolytic hydrocarbons were expelled during the early heating stages. In Stages III–IV, organic matter was converted into oil and gas, and a large amount of hydrocarbons was expelled; the conversion rates of S_2 into oil and gas were as high as 97.18%, 96.19%, and 96.32%, respectively. Consequently, the S_2 values decreased rapidly and remained low during the later heating stages.

$S_1 + S_2$ represents the total amount of hydrocarbons that have been generated but not expelled, together with the potential hydrocarbons that can still be produced in the sample, and is referred to as the hydrocarbon generation potential. This parameter is an indicator for evaluating the richness of organic matter in the rock [30]. The hydrocarbon generation potential of the three original samples (FS, MH, and HD) was 178.10 mg/g, 112.17 mg/g, and 116.21 mg/g, respectively. The hydrocarbon generation potential of the three groups of samples showed a relatively consistent trend, gradually decreasing with increasing temperature. However, the phenomenon of S_1 increasing and S_2 decreasing appeared in Stage III, indicating that this heating stage was an important hydrocarbon generation interval.

3.3. Industrial indicators

3.3.1. Ash content

Ash content is the mass of residue remaining after the complete combustion of oil shale per unit mass at 810 °C [31]. The ash content of oil shale is an important indicator for distinguishing oil shale from coal and is also an important parameter for evaluating the quality of oil shale. Generally, the lower the ash content of oil shale, the higher the organic matter content and the better the quality of the oil shale.

The ash yield of MH oil shale was the highest at 74.6 wt%, followed by FS oil shale at 64.0 wt%, while HD oil shale had the lowest ash yield at 57.1 wt%. The ash yields of the three oil shale samples showed a consistent trend, increasing gradually with increasing temperature. The ash contents of the FS, MH, and HD samples increased by 9.5 wt%, 4.3 wt%, and 9.0 wt%, respectively, all showing significant increases in Stages II–IV (Table 4 and Fig. 5).

Table 4. Characteristics of oil shale ash yield changes at different heating stages

Basin	Sample	Original sample	Ash yield, wt%					
			I	II	III	IV	V	VI
Fushun Basin	FS	64.0	64.7	65.3	70.7	80.2	81.1	81.9
Meihe Basin	MH	74.6	74.8	75.8	76.9	81.2	84.4	84.7
Huadian Basin	HD	57.1	57.5	60.4	63.8	72.8	73.7	74.3

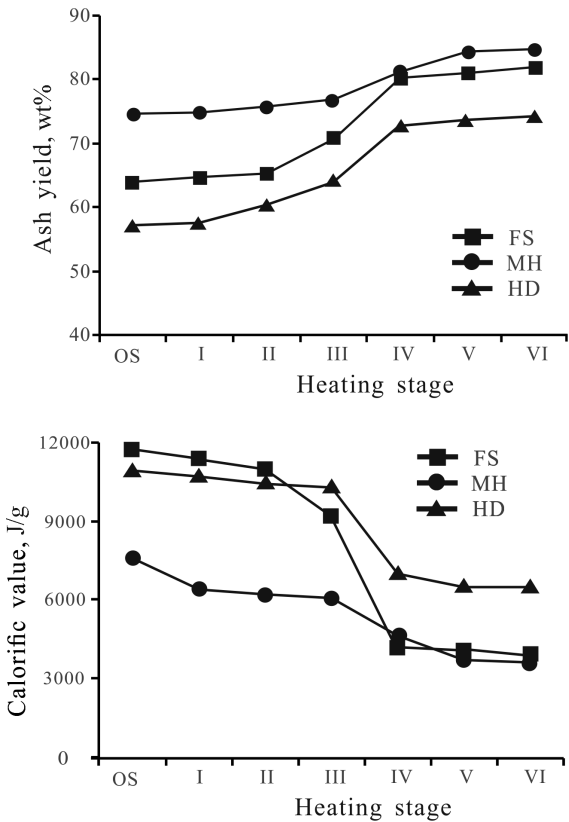


Fig. 5. Ash yield and calorific value at different heating stages of oil shale.

Calorific value is an important indicator in the industrial analysis of oil shale. The calorific values of oil shale and its residues can be used to reasonably evaluate the comprehensive utilization of oil shale, which is a favorable approach to improving the benefits of oil shale exploitation and utilization and enhancing environmental protection [32].

The FS oil shale had the highest calorific value, reaching 11744 J/g, followed by the HD and MH oil shale with 10933 J/g and 7605 J/g, respectively. The calorific values of the three groups of samples showed a decreasing trend with heating, with a significant decline in Stages III–IV, where the calorific values of FS, HD, and MH decreased by 4919 J/g, 3276 J/g, and 1451 J/g, respectively (Table 5 and Fig. 5), which corresponds to the highest energy release efficiency during the conversion of organic matter into hydrocarbons.

Table 5. Characteristics of oil shale calorific value changes at different heating stages

Basin	Sample	Original sample	Calorific value, J/g					
			I	II	III	IV	V	VI
Fushun Basin	FS	11744	11377	11000	9182	4263	4050	3909
Meihe Basin	MH	7605	6402	6200	6082	4631	3700	3595
Huadian Basin	HD	10933	10686	10409	10263	6987	6498	6493

4. Discussion

4.1. Organic matter hydrocarbon generation characteristics at different heating stages

During Stages I–II, TOC varied moderately and hydrocarbon generation potential decreased slightly. This indicates that oil shale samples were dominated by water production with negligible oil generation at these stages, featuring minimal organic matter loss and high organic matter abundance. It also demonstrates that large-scale hydrocarbon generation and expulsion had not yet occurred at these heating stages.

During Stages III–IV, substantial amounts of oil and water were expelled, TOC dropped sharply, and the conversion rate of S_2 to hydrocarbons reached as high as 96%. These phenomena suggest that large quantities of organic matter were consumed and converted into hydrocarbons at these stages, corresponding to the primary hydrocarbon generation window.

During Stages V–VI, there was basically no oil or water production, but TOC decreased slightly and gas loss increased. This reveals that the remaining consumable organic matter was almost entirely converted into gas at these stages, marking the end of organic matter hydrocarbon generation and expulsion.

The final residual organic carbon content retained in the samples ranged from 9.6 wt% to 14.5 wt%. The hydrocarbon generation conversion rates of the FS, HD, and MH samples were 97.96%, 98.27%, and 97.95%, respectively. This shows that even after complete hydrocarbon generation and expulsion, a large amount of residual organic matter still remained in the oil shale. This change pattern can provide effective parameters for the recovery of highly mature hydrocarbon source rocks.

According to the organic matter type discrimination diagram, FS contains type I kerogen, while MH and HD contain type II kerogen (Fig. 6). The thermal evolution trends of organic matter in the three samples were similar, and all the original samples were in the under-mature stage. The residues in Stages I–III were in the low-maturity to mature stage; the residues in Stage IV were in the wet gas stage, and the residues in Stages V–VI were in the over-mature stage.

A comparison reveals certain differences in the hydrocarbon generation process between type I kerogen samples (FS) and type II kerogen samples (MH and HD). In terms of oil production efficiency, the total oil yield of FS samples (15.5 wt%) was 72–80% higher than that of the HD and MH samples (8.6–9.0 wt%). The increase in oil yield during Stages III–V (10.2 wt%) was 1.9–2.0 times that of the type II kerogen samples (5.1–5.3 wt%).

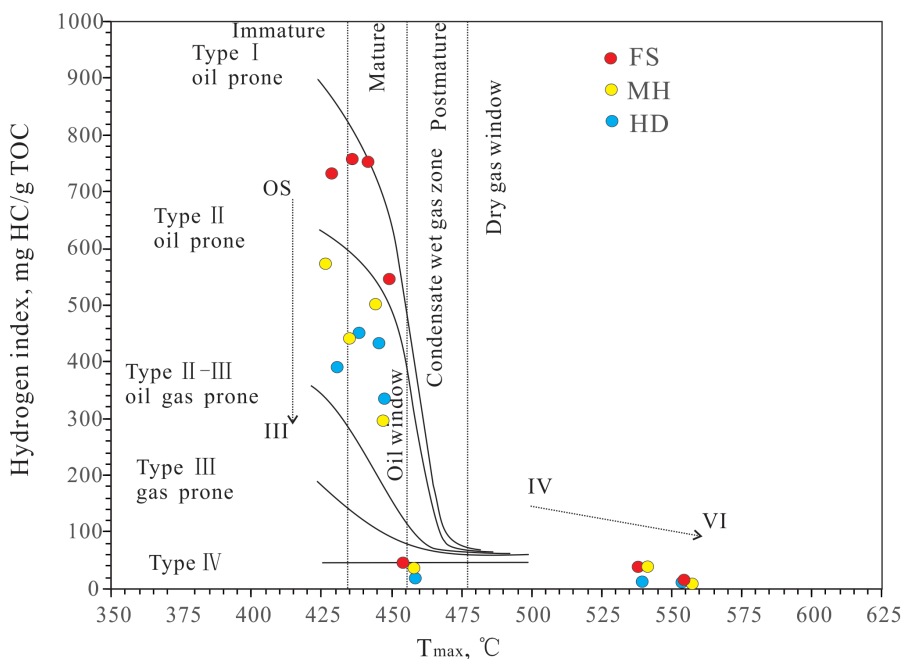


Fig. 6. Organic matter type discrimination at different heating stages.

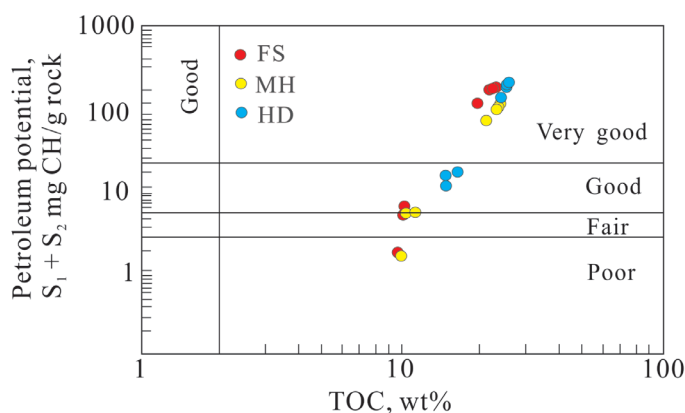
In terms of temperature sensitivity, the oil yield of the type I kerogen samples showed explosive growth after 400 °C, whereas that of the type II kerogen samples increased relatively moderately. Additionally, the S_2 hydrocarbon conversion rate of type I kerogen samples (97.18%) was slightly higher than that of the type II kerogen samples (96.19–96.32%). In terms of attenuation of hydrocarbon generation potential, the attenuation rate of the HI value for the type I kerogen samples was higher than that for the type II kerogen samples, reflecting that type I kerogen was more prone to achieving efficient conversion under rapid temperature rise.

4.2. Evolutionary law of hydrocarbon generation potential at different heating stages

The hydrocarbon potential (TOC) and HI–TOC diagrams (Fig. 7) show that the hydrocarbon potential of the three groups of samples exhibited significant regular changes at different heating stages.

At the original sample–Stage II interval, the hydrocarbon potential of the three oil shale samples was classified as very good, indicating excellent oil source rock quality (Fig. 7). This indicates that oil shale retained high hydrocarbon potential during the initial stage of heating. The HI–TOC diagram further shows that oil shale remained an extremely high-quality source rock even after being treated at lower heating temperatures.

During Stages III–IV, the hydrocarbon potential of the FS, MH, and HD oil shale samples decreased from very good to good (Fig. 7), indicating that with increasing heating temperature, oil yield rose significantly, leading to a decrease in oil shale quality. The HI–TOC diagram shows that the oil shale transitioned from an oil or gas source rock to a gas source rock at these stages. It is noteworthy that the oil shale samples still retained good hydrocarbon potential after being heated to 400 °C, indicating that this temperature could not completely convert the remaining organic carbon into oil.



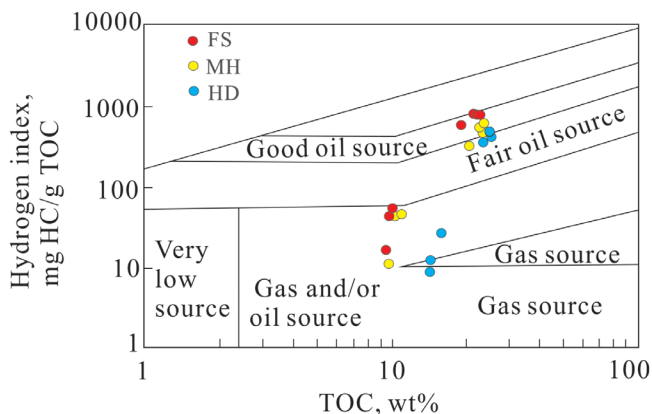


Fig. 7. Hydrocarbon potential discrimination of residues at different heating stages of oil shale [33–34].

During Stages V–VI, no oil was produced, but some gas was generated. This indicates that the hydrocarbon potential of the oil shale samples at these heating stages was poor, although some residual organic carbon remained (Table 2 and Fig. 7). At this point, the samples became poor oil or poor gas source rocks, with almost no hydrocarbon potential (Fig. 7). The remaining organic carbon, despite having no hydrocarbon potential, could act as a self-heating carrier to provide a heat source for surrounding oil shale that had not yet undergone hydrocarbon conversion.

5. Conclusions

Open-system thermal simulation of the three oil shale samples showed that the evolution characteristics of the products can be divided into three distinct stages:

1. During the initial heating stages I–II, the oil yield and gas yield of the oil shale samples were both low, with the main products being water and a small amount of gas, and the hydrocarbon generation potential of the residue was excellent. In the heating stages III–IV, a large amount of organic carbon in the oil shale samples was consumed, resulting in a large amount of oil and gas, and the hydrocarbon generation potential of the residue rapidly decreased from excellent to good. In the heating stages V–VI, water and oil yields stabilized, gas yield increased slightly with dry gas as the dominant organic gas, and the hydrocarbon generation potential gradually deteriorated to poor.
2. Analysis of the $T_{\max}$ –HI cross plot reveals that Fushun oil shale is dominated by type I kerogen with the highest oil generation efficiency,

whereas Huadian and Meihe oil shale samples are primarily composed of type II kerogen with relatively reduced oil generation capacity, indicating that organic matter type exerts a significant influence on hydrocarbon generation efficiency.

3. Organic matter enters the oil generation window at 300 °C and reaches the peak hydrocarbon expulsion stage at approximately 475 °C. Based on the characteristics of organic matter conversion efficiency and the hydrocarbon generation window, the temperature range of 400–475 °C is tentatively proposed as the optimal heating interval for in-situ conversion of oil shale, enabling maximum hydrocarbon output with minimal organic matter consumption.

Data availability statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

Acknowledgments

This research was supported by funding from the Major National Science and Technology Project for New Oil & Gas Exploration and Development, “Oil and Gas Enrichment Regularities and New Field Exploration Technologies in the Bohai Bay Super Basin” (No. 2024ZD1400100). The publication costs of this article were partially covered by the Estonian Academy of Sciences.

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Exploring the influence of heating rate on the permeability of Fushun oil shale

Zihao Lu^(a), Yanchao Wang^(a), Jinjie Huo^(b), Yi Pan^{(a)*}, Shuangchun Yang^(a), Jiabing Zheng^(c)

^(a) College of Petroleum and Natural Gas Engineering, Liaoning Petrochemical University, Fushun, Liaoning 113001, China

^(b) Central Asia Research Institute, Xinjiang Oilfield Exploration and Development Research Institute, Xinjiang 834000, China

^(c) Exploration and Development Science Academy, Zhongyuan Oilfield Company, Sinopec, 457001, China

Received 5 January 2026, accepted 21 October 2026, available online 23 October 2026

Abstract. Oil shale from the Fushun West Open-pit Mine was selected as the research object to study the influence of heating rate on permeability. Through pyrolysis experiments at different heating rates, the evolution of permeability under various heating conditions was explored. Response surface methodology was used to optimize the pyrolysis parameters, and the optimal parameter combination was determined: a heating rate of 34.55 °C/min, a final reaction temperature of 475 °C, and a constant-temperature holding duration of 131 min. Under these conditions, the pyrolysis efficiency of Fushun oil shale was optimal. The key parameters identified provide a valuable reference for the in-situ exploitation of Fushun oil shale.

Keywords: oil shale, heating rate, permeability, response surface optimization.

1. Introduction

The 2025 international Unconventional Resources Technology Conference (URTeC) highlights that unconventional resources, particularly oil shale, provide lasting solutions to global energy challenges. Green and high-value utilization has become the core orientation [1].

In terms of advanced mining technologies, Pan et al. [2] and Li et al. [3] summarized sophisticated approaches such as the in-situ conversion process (ICP), geothermal fuel cell (GFC) technology, supercritical water heating (SWH), and voltage-induced fracturing. Crucially, Liu et al. [4] proved that

* Corresponding author, panyi_beijing@163.com

these technologies drive pore network evolution through fundamentally distinct mechanisms. For conductive heating, Zhao et al. [5] experimentally confirmed that ICP's slow heating triggers massive mineral decomposition at 350 °C, increasing porosity up to tenfold. Similarly, Luo et al. [6] found that GFC's steady mid-temperature heat transforms isolated pores into a highly connected bimodal network with a peak pore size of 15.2 nm. Conversely, for convective heating, Kang et al. [7] reported that SWH utilizes hydrothermal effects to extract pore-blocking bitumen and catalyze clay illitization, generating fractures up to 150 μm wide – five times larger than those generated by dry pyrolysis. Finally, Bauer et al. [8] demonstrated that voltage-induced fracturing uses electromechanical shockwaves to physically shatter the rock matrix, creating macro-scale channels that resist closure under a 58.6 MPa hydrostatic pressure and increase permeability by up to nine orders of magnitude. Consequently, optimizing fluid migration requires quantifying how specific heating rates and thermodynamic parameters drive this microscopic structural evolution under each distinct technology.

In terms of experiments and simulations, although oil shale holds great promise, research on how heating rates impact its macroscopic permeability remains insufficient. The permeability enhancement generally transitions from a pore-structure-dominated regime at low temperatures to a fracture-dominated regime at high temperatures [9–10]. Schrodtt et al. [11] studied the effect of the heating rate on the pore structure of U.S. oil shale using nitrogen and carbon dioxide as pyrolysis atmospheres. The results indicated that during the low-temperature stage of the reaction (< 300 °C), hot gas products precipitated to a certain extent to fill the pore volume, and the pore area decreased. At high temperatures (300–600 °C), the pore area increased significantly, while the pore surface area changed little at different heating rates. Sun et al. [12] analyzed the evolution of pores and fractures in the pyrolysis solids of oil shale using nitrogen isothermal adsorption experiments. With increasing heating rate, micropores and mesopores formed fractures that developed into fracture networks. Li et al. [13] and Yu et al. [14] simulated in-situ extraction conditions, demonstrating that optimizing the heating temperature is vital for hydrocarbon generation and fracture propagation. Recently, increasing attention has been paid to Fushun oil shale to investigate its thermal cracking characteristics and dynamic permeability evolution [7].

Liu et al. [4] comprehensively reviewed the thermal cracking process, pore evolution, and permeability enhancement of oil shale under various in-situ heating conditions. To further observe the internal structural changes, Zhang et al. [15] utilized advanced computed tomography imaging techniques to characterize how temperature and heating media influence the mesostructural evolution of fractured shale during in-situ pyrolysis. Additionally, Abdi-Khanghah et al. [16] employed non-isothermal kinetic modeling to optimize the thermodynamic parameters for maximizing the hydrocarbon yield of shale reservoirs. However, as pointed out by Yang et al. [17], while the fundamental mechanisms of pyrolysis and fracture generation have been

widely documented, comprehensive studies quantitatively evaluating the coupled effects of different heating rates on macroscopic permeability remain limited [18].

In view of the above factors, relevant experimental studies on the influence of heating rates, as well as parameter optimization based on response surface methodology (RSM), are currently lacking. Therefore, it is necessary to design pyrolysis experiments using Fushun oil shale to obtain the variation in permeability under different heating rates. By applying RSM to establish a predictive quadratic regression model, we aim to determine the optimal parameter combinations required to maximize fluid migration capacity. This study provides a reference for investigating temperature-dependent behavior in the field of in-situ oil shale extraction.

2. Experimental study on the permeability of Fushun oil shale at different heating rates

2.1. Experimental materials, instruments, and samples

Oil shale from the Fushun West Open-pit Mine was used as the experimental material, and mixed oil shale samples extracted from each quarter were used. Fushun oil shale originates from the Fushun area of Liaoning Province in northern China. The mineral composition includes kaolinite, montmorillonite, illite, calcite, pyrite, etc., and the surface is rich in bituminous luster. Fushun oil shale has a high organic carbon content, with a maximum oil content of up to 12% and an average oil content of around 5% to 8%. Fushun oil shale is rich in Al_2O_3 and SiO_2 and has a high melting point.

Experimental measurements of oil shale permeability at different heating rates were conducted, and the instruments and equipment used in the experiments are shown in Table 1.

Table 1. Experimental equipment

Device	Equipment model	Manufacturer
Digital display forced air drying oven	GZX-9023 MBE	Shanghai Boxun Industrial Medical Company
Electronic analytical balance	BSA223S+	Beijing Sartorius Instruments Co., Ltd.
Automated dust-free core preparation equipment	KDZQGM-II	Jiangsu Kedi Petroleum Instrument Co., Ltd.
Permeability meter	STY-II gas permeability meter	Nantong Huaxing Petroleum Instrument Co., Ltd.
Muffle furnace	SXL-1008 Programmable box-type electric furnace	Shanghai Jinghong Laboratory Instrument Co., Ltd.

Before the experiment, the samples were processed. The samples were cut into cylindrical cores with a diameter of 50 mm and a length of 20 to 70 mm using a drilling machine. A total of 18 sets of experiments were conducted. The oil shale cores were then dried in an oven at 105 °C for 24 hours and subsequently placed in a desiccator to cool to room temperature.

2.2. Experimental methodology

2.2.1. Experimental conditions

Oil shale core samples were pyrolyzed at different heating rates, and the permeability of the cores was measured at each temperature point. The heating rates were set at 10, 20, 30, 40, 50, and 60 °C/min, and the pyrolysis temperature points were set at 300, 400, 500, and 600 °C.

2.2.2. Preparation of the permeability instrument

- Measure the core sample length and diameter with a vernier caliper and calculate the cross-sectional area A .
- Insert the standard core block into the core holder and turn the hand wheel upward until the top of the sample fits tightly against the top of the holder and is securely fixed.
- Connect the nitrogen cylinder. Open the gas source valve (the gas source pressure is pre-adjusted) and open the ring pressure valve (the ring pressure is pre-adjusted). After the pressure on the ring pressure gauge stabilizes, close the ring pressure valve.
- Adjust the pressure-regulating valve. When the pressure gauge reaches the pressure required for the experiment, open the measuring valve and read the float flowmeter flow at different pressures.
- Adjust the pressure-regulating valve to zero pressure, vent through the ring pressure valve to zero ring pressure, and then repeat the above steps to remove the rock sample.

A diagram of the core permeability measurement system is shown in Figure 1.

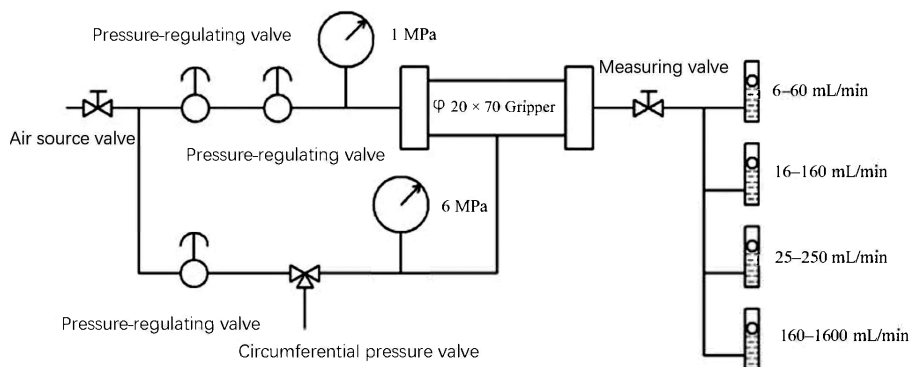


Fig. 1. Schematic diagram of the permeability measurement system.

2.2.3. Experimental procedure

- Record the core sample dimensions (diameter D , length L , and cross-sectional area A) and the experimental conditions (gas viscosity μ , chamber temperature t , and atmospheric pressure P_a). Permeability was calculated from the measured pressure drop and flow rate using Darcy's law.
- Since actual measurements are influenced by pressure and temperature variations, and given the high compressibility and thermal expansion of gases in the measurement environment, flow rate correction is necessary. Specifically, one of the four miniature float flowmeters (with different measurement ranges) equipped with the gas permeability meter should be selected during measurements. Where conditions permit, the flowmeter with the smallest applicable range is preferred. The calculation formula is as follows:

$$Q_0 = 0.2853Q'_0 \sqrt{\frac{1}{p_a(273 + t) \times 10}}, \quad (1)$$

where Q_0 is the corrected actual flow rate, Q'_0 is the flowmeter reading, P_a is the absolute atmospheric pressure, and t is the room temperature.

- Record the pressures P_1 and P_2 at both ends of the core as gas flows through it, then calculate the average pressure ($\bar{P} = (P_1 + P_2)/2$) and record the gas volumetric flow rate ($\bar{Q}$). Finally, substitute these parameters into Darcy's formula.

The percolation law of a unidirectional fluid through the core only conforms to Darcy's law when the pressure gradient is small and the flow rate is low. When the pressure gradient exceeds this limit, it no longer follows Darcy's law but instead follows a nonlinear percolation law. The results are described by Equation 2:

$$k_g = \frac{2Q_2L\mu p_0}{A(p_1^2 - p_2^2)} \times 10^{-1}, \quad (2)$$

where k_g is the gas permeability, Q_2 is the gas flow rate at the core outlet end, L is the core length, μ is the gas viscosity at test temperature and atmospheric pressure, P_0 is the atmospheric pressure, A is the cross-sectional area of the core, P_1 is the absolute pressure at the core inlet end, and P_2 is the absolute pressure at the core outlet end.

2.3. Results of the oil shale permeability test

The pyrolysis environment was monitored by recording core pressures and flow rates, with permeability calculated using Darcy's law (Fig. 2). Permeability exhibits a phased growth trajectory as temperature increases.

Phase I: Pore-structure-dominated evolution (20–300 °C): Permeability remains extremely low. Minor fluctuations driven by water evaporation and thermal expansion create isolated micro-pores that lack the connectivity needed for effective fluid migration.

Phase II: Fracture-dominated evolution (300–500 °C): An exponential surge in permeability occurs. Above 380 °C, intense kerogen pyrolysis generates massive amounts of volatile hydrocarbons, causing localized fluid overpressure that forcefully drives rapid micro-fracture propagation.

Phase III: Mineral-transformation-supported evolution (500–600 °C): With organic pyrolysis nearly complete, explosive permeability growth decelerates. Further minor enhancements are sustained primarily by mineral phase transformations.

In summary, the macroscopic permeability evolution of Fushun oil shale is fundamentally fracture-dominated. Organic matter pyrolysis is the absolute dominant driver, creating severe fluid overpressure that shatters the rock matrix to exponentially increase permeability. Conversely, mineral transformations play only a secondary, auxiliary role, sustaining slow permeability increases at extremely high temperatures (500–600 °C).

The change in permeability is mainly due to the uneven thermal expansion of special mineral matrices and high-temperature thermal reactions, such as the dehydroxylation of kaolinite at around 550 °C and of illite at around 580 °C. With the extension of pyrolysis time, the temperature of the oil shale core becomes sufficient to meet the pyrolysis conditions, and the uneven thermal stress within the core also causes fractures to expand and penetrate. As a result, the internal damage to the oil shale increases, and thermal fractures develop along the bedding direction. All these factors combined cause the permeability to increase slowly.

Regarding the effect of the heating rate on permeability, the experimental data reveal a non-linear evolutionary trend. In the active pyrolysis zone (400–500 °C), Yang et al. [17] demonstrated that higher heating rates induce more severe thermal shock and elevated temperature gradients, generating higher localized fluid overpressures that forcefully accelerate micro-fracture propagation. However, as the temperature approaches 600 °C, the correlation between heating rate and permeability enhancement shows no obvious trend. This plateau occurs because the primary organic matter has been completely exhausted, and permeability is now governed by competing secondary geomechanical mechanisms rather than volatile gas expansion. For instance, Li et al. [3] indicated that high temperatures and secondary reactions within the pores can lead to coke formation, which risks blocking narrow seepage channels. Furthermore, Zhao and Kang [19] experimentally confirmed that the extensive generation of fractures during the main pyrolysis phase severely compromises the compressive strength of the inorganic mineral skeleton, causing some unproped micro-fractures and pores to collapse or close under stress. Consequently, the ultimate permeability at 600 °C is dictated by the maximum structural damage sustained during the 400–500 °C phase and subsequent high-temperature mineral softening, rather than by the ongoing heating rate.

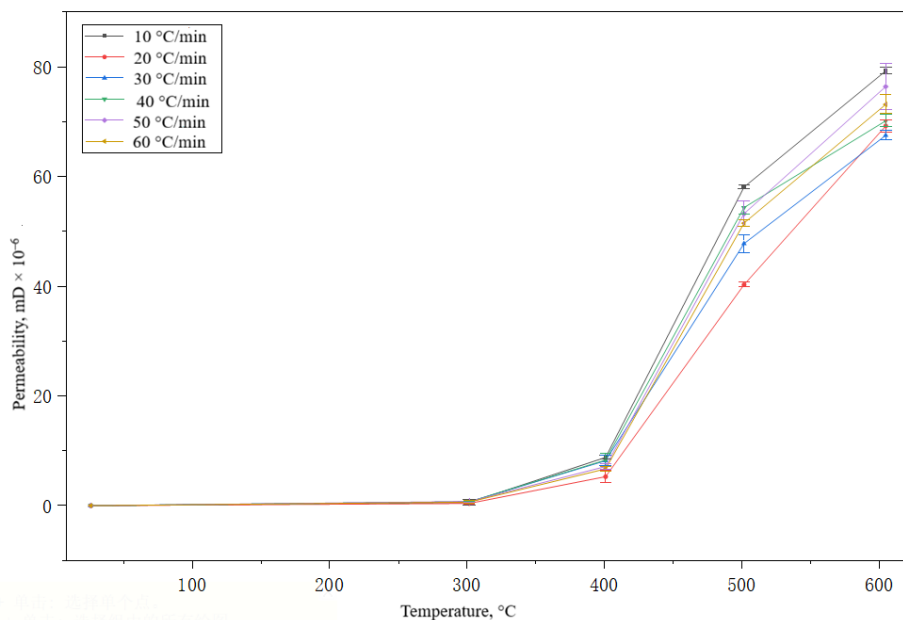


Fig. 2. Permeability curves of oil shale varying with temperature at different heating rates.

The oil shale samples are uniform and dense in their natural state before pyrolysis. With the increase in temperature, the decomposition of organic matter and the precipitation of inorganic minerals, the oil shale is more likely to develop cracks in the horizontal layer and connect and expand, resulting in significant changes in sample appearance and color. As the temperature reaches 300 °C, effective oil and gas seepage channels are formed along the horizontal bedding direction. The morphological changes of the core at temperatures of 20, 300, 400, 500, and 600 °C, including prominent features such as fracture propagation and structural fragmentation throughout the pyrolysis process, are presented in Figures 3 and 4.

The entire process shows a progressive trend of microfracture formation → local expansion → multidirectional development → local fracture → fracture expansion → reticular fracture → deep extension → complete dissociation, with fractures gradually evolving from surface damage to penetrating failure, accompanied by changes in the core structure from an intact state to complete fragmentation.

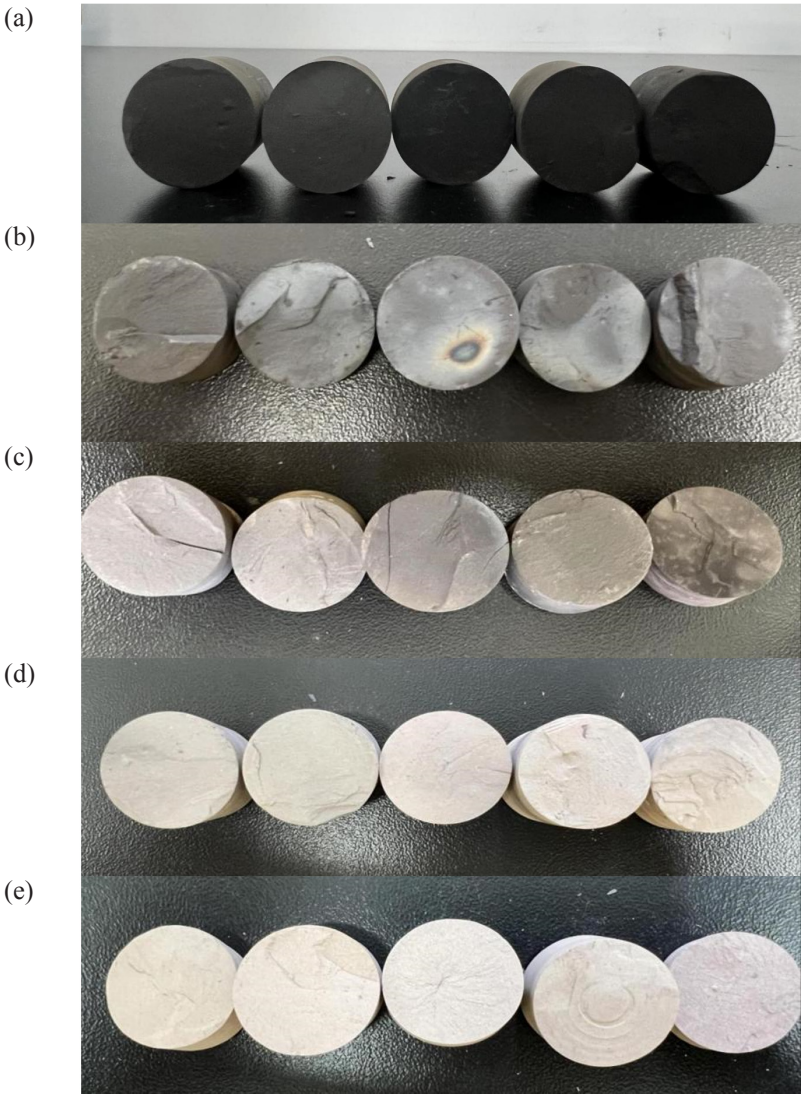


Fig. 3. Comparison of core sample states at different temperatures: (a) 20 °C, (b) 300 °C, (c) 400 °C, (d) 500 °C, and (e) 600 °C.

Note: To indicate the spatial scale, the standardized diameter of all cylindrical core samples shown in the images is exactly 50 mm, which serves as an internal scale reference. The lengths range from 20 mm to 70 mm.



Fig. 4. Core fracture propagation networks and structural failure conditions highlighting: (a) horizontal bedding expansion, and (b) vertical bedding fracture intersections.

Note: To indicate the spatial scale, the standardized diameter of all cylindrical core samples shown in the images is exactly 50 mm, which serves as an internal scale reference. The lengths range from 20 mm to 70 mm.

3. Analysis of pyrolysis data based on the response surface

3.1. Response variable – permeability optimization design

The pyrolysis experiments were conducted using multiple heating rates to test the permeability of the oil shale and optimize the response surface design. The heating rates were set at 10, 20, 30, 40, 50, and 60 °C/min to control the ambient temperature changes, and the final pyrolysis temperatures were set at 300, 400, 500, and 600 °C. After reaching the final pyrolysis temperature, the samples were maintained at a constant temperature for 0.5, 1, 2, and 3 h, respectively, followed by an optimization analysis of the permeability.

The optimized design approach was as follows. An experimental design was developed to optimize the permeability response surface with regard to the three response variables: heating rate, final pyrolysis temperature, and constant-temperature duration. A mathematical model was established using the Box–Behnken center combinatorial experimental design for response surface analysis. The quadratic multiple regression equation for oil shale pyrolysis permeability (Y_3) as a function of the independent variables A, B, and C is given in Equation 3.

To ensure absolute analytical clarity and mathematical consistency, the three critical independent variables are explicitly defined as follows:

Variable A: heating rate (°C/min)

Variable B: final pyrolysis temperature (°C)

Variable C: constant-temperature duration (h)

$$Y_3 = 1.345 \times 10^{-5} + 7.916 \times 10^{-7} A + 3.512 \times 10^{-5} B - 5.33 \times 10^{-6} C + 3.290 \times 10^{-6} AB + 2.347 \times 10^{-5} AC - 4.608 \times 10^{-6} BC - 1.171 \times 10^{-5} A^2 + 2.525 \times 10^{-5} B^2 - 8.708 \times 10^{-6} C^2 \quad (3)$$

The significant lack of fit (LOF) in Table 2 is a recognized statistical artifact known as the low pure-error phenomenon, in which the test becomes hypersensitive due to minimal replicate variance. The extreme precision of the permeability measurement equipment yielded near identical center-point replicates, driving the pure-error variance close to zero. Since this variance serves as the denominator of the LOF calculation, its minute size artificially inflates the F value, causing a false-positive significance result. However, aligned with Quality by Design principles for robust process optimization, the model's high R^2 value (0.9482) confirms that this mathematical anomaly does not compromise its predictive reliability [20, 21].

The results of the significance analysis are shown in Table 2. The model P value < 0.0001 indicates that the relationship among the model variables is extremely significant. The regression equation accurately reflects the relationship between permeability evolution and the thermodynamic factors. Based on the analysis of variance outcomes, the primary hierarchy of influence exerted by the three independent variables on the terminal pyrolysis permeability of the oil shale is: B (final pyrolysis temperature) > A (heating

rate) > C (constant-temperature duration). The extreme statistical significance of variable B directly corroborates the physical mechanistic observation that breaking the thermal activation threshold for kerogen pyrolysis is the absolute dominant driver of extensive fracture generation. This conclusion is consistent with the order of the three response variables in terms of weightless physical properties. The response surface analysis is shown in Figure 5.

Table 2. Regression model variance analysis results

Source	Sum of squares	Degrees of freedom	Mean square	F value	P value	Significance
Model	8.607×10^{-9}	9	9.564×10^{-10}	14.25	<0.0001	Significant
A	1.957×10^{-12}	1	1.957×10^{-12}	1.92	0.2082	
B	4.137×10^{-9}	1	4.137×10^{-9}	61.64	<0.0001	
C	1.290×10^{-10}	1	1.290×10^{-10}	0.029	0.7128	
AB	2.035×10^{-12}	1	2.035×10^{-12}	0.003	0.8667	
AC	1.103×10^{-10}	1	1.103×10^{-10}	1.64	0.2408	
BC	3.626×10^{-11}	1	3.626×10^{-11}	0.54	0.4862	
A2	1.446×10^{-10}	1	1.446×10^{-10}	2.15	0.1856	
B2	4.726×10^{-10}	1	4.726×10^{-10}	7.04	0.0328	
C2	3.410×10^{-11}	1	3.410×10^{-11}	0.51	0.4991	
Lack of fit	4.69	7	6.712×10^{-11}		0.0021	Significant
Pure error	9.077×10^{-9}	16				

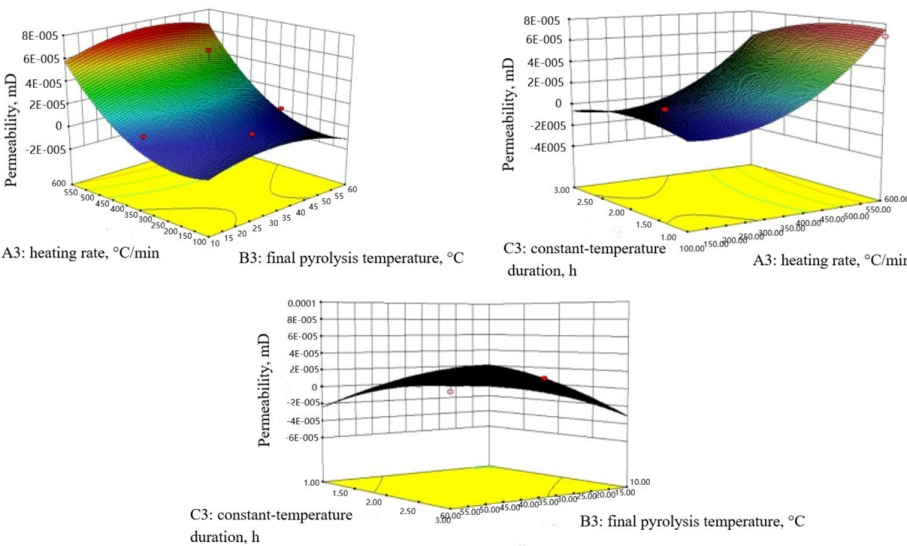


Fig. 5. Response surface analysis of the factors influencing the pyrolysis permeability of oil shale.

3.2. Determination and validation of the optimal heating rate

The optimal pyrolysis environment for the physical parameters of oil shale pyrolysis was obtained by analyzing the experimental results using Design-Expert software. The heating rate should be controlled at 34.55 °C/min, the optimal final temperature of the pyrolysis reaction should be 475 °C, and the duration of maintaining a constant temperature until the final temperature of pyrolysis is 131 min. The predicted permeability value is 7.903×10^{-5} mD.

To verify the validity of the model, based on the actual conditions, the pyrolysis conditions were modified according to the optimized response data with a heating rate of 35 °C/min, a final temperature of 480 °C, and a constant temperature duration of 130 min. Under these conditions, to ensure the validity of the experiment, three pyrolysis experiments were conducted to verify the response values and calculate the average. The experimentally measured post-pyrolysis permeability of the oil shale was 7.075×10^{-5} mD. The extremely high concordance between this physical validation measurement and the theoretical response prediction solidly compensates for the statistical lack-of-fit outcome, providing empirical proof that the regression model is highly reliable for optimizing operational parameters.

4. Conclusions

Fushun oil shale was studied to investigate the effects of different heating rates (10, 20, 30, 40, 50, and 60 °C/min) on the physical properties of Fushun oil shale. First, the pyrolysis characteristics of Fushun oil shale at different heating rates were analyzed. Second, the permeability response was optimized to obtain the optimal heating rate affecting the pyrolysis of oil shale. The following conclusions are drawn:

1. The permeability evolution of Fushun oil shale exhibits a distinct, non-linear dynamic that is heavily dependent on thermal thresholds. Below 300 °C, permeability alterations remain negligible and are primarily pore-structure-dominated, driven by localized mineral expansion and moisture evaporation. Conversely, between 400 °C and 500 °C, the massive decomposition of kerogen induces severe fluid overpressure, violently shifting the matrix into a fracture-dominated regime characterized by exponential permeability enhancement through penetrating fracture networks. Above 500 °C, mineral phase transformations contribute to auxiliary crack propagation.
2. The primary order of the effects of each factor on permeability is final pyrolysis temperature > heating rate > constant-temperature duration
3. Based on the established novel quantitative prediction model, the optimal environmental control parameters were as follows: a heating rate of 34.55 °C/min, an optimal final pyrolysis temperature of 475 °C, and a constant-temperature duration of 131 min. The predicted pyrolysis permeability of the oil shale obtained was 7.903×10^{-5} mD.

Data availability statement

The datasets generated and analyzed during this study are available from the corresponding author upon reasonable request.

Acknowledgments

Yanchao Wang conceptualized the study. Jinjie Huo and Shuangchun Yang validated the methodology, while Jinjie Huo conducted the investigation. Jinjie Huo and Shuangchun Yang provided the resources, and Jinjie Huo and Yi Pan curated the data. Jinjie Huo and Zihao Lu prepared the original draft of the manuscript, which was reviewed and edited by Zihao Lu and Shuangchun Yang. Shuangchun Yang and Yi Pan supervised the study, and Jiabing Zheng revised the manuscript. All authors have read and agreed to the published version of the manuscript. This work was supported by the National Science Foundation of China (NSFC) (grant No. 52574041) and the Liaoning Province Science and Technology Joint Program (2025JH2/101800421). The publication costs of this article were partially covered by the Estonian Academy of Sciences.

Nomenclature

Symbol	Description	Unit
β	Heating rate	$^{\circ}\text{C}/\text{min}$
D	Core diameter	cm
L	Core length	cm
A	Core cross-sectional area	cm^2
Q_0	Actual flow rate	ml/s
Q'_0	Flowmeter reading	ml/min
P_a	Absolute atmospheric pressure	MPa
k_g	Gas permeability	mD
μ	Gas viscosity at the test temperature and atmospheric pressure	$\text{mPa}\cdot\text{s}$
t	Room temperature	$^{\circ}\text{C}$
Y_3	Oil shale pyrolysis permeability	mD
A	Independent variable (heating rate) in response surface optimization	$^{\circ}\text{C}/\text{min}$
B	Independent variable (final pyrolysis temperature) in response surface optimization	$^{\circ}\text{C}$
C	Independent variable (constant-temperature duration) in response surface optimization	h
P_1	Absolute pressure at the core inlet	MPa
P_2	Absolute pressure at the core outlet	MPa

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Coupling of sedimentary environment and hazardous trace element enrichment in lacustrine oil shale: evidence from the Lunpola Basin, Tibetan Plateau, China

Yansheng Shan^(a), Shuai Zhang^{(a)*}, Ying Nie^(a), Tenghui Lu^{(b)*}

^(a) Oil and Gas Survey, China Geological Survey, Beijing 100083, China

^(b) School of Geoscience and Technology, Southwest Petroleum University, Chengdu 610500, China

Received 6 February, accepted 21 October 2026, available online 23 October 2026

Abstract. *The Lunpola Basin, developed during the Cenozoic era on the Tibetan Plateau, serves not only as a sedimentary record of plateau uplift but also as a significant reservoir of oil shale. This study focuses on the sedimentary environment of the oil shales in the Lunpola Basin and the enrichment mechanisms of trace elements, particularly hazardous elements, within them. A total of 38 samples were analyzed for major elements, trace elements, total organic carbon (TOC), and total sulfur (TS). Results show that several elements are significantly enriched relative to upper continental crust values, notably As (up to 45×), Mo (5.2×), Pb (3.8×), and U (3.3×). Geochemical proxies indicate deposition in a brackish to saline lacustrine setting, under predominantly anoxic to suboxic conditions, and in a warm–humid paleoclimate with moderate to low weathering intensity. Correlation analysis reveals that hazardous elements (As, Mo, Pb, U) are positively associated with TOC and TS, suggesting that organic matter and sulfide phases play key roles in their enrichment. Redox conditions appear to exert a primary control, while salinity and clay minerals contribute to secondary regulation. These results indicate that the enrichment of hazardous elements in the Lunpola oil shales is controlled by a combination of depositional environment and organic matter preservation, providing new insights into element cycling in continental lacustrine systems and implications for environmental risk during oil shale exploitation.*

Keywords: oil shale, potentially hazardous elements, trace elements, paleoenvironment, Lunpola Basin.

* Corresponding authors, zhangshuai870517@163.com, lutenghui2000@126.com

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1. Introduction

Oil shale stands as a critically important unconventional energy resource in China, underpinned by its vast reserves and relatively mature extraction technologies [1, 2]. However, its development potential is closely constrained by a range of environmental concerns, particularly those related to the enrichment, mobilization, and potential release of toxic and hazardous trace elements (e.g., As, Cd, Pb, U) during mining, retorting, and waste disposal processes, which may pose long-term risks to surrounding soil, water systems, and ecosystems [3, 4]. In the context of the ongoing transition away from fossil fuels, understanding the occurrence states, enrichment patterns, and potential release risks of trace elements, especially toxic and hazardous elements, within oil shale is paramount for ensuring the environmental sustainability of resource exploitation [5].

The Lunpola Basin in Tibet hosts substantial Miocene oil shale sequences. Among these, the deposits found in the Lunpori area represent the largest known oil shale resource on the Tibetan Plateau [6]. These deposits also serve as a unique natural archive for studying the coupled processes of plateau uplift, paleoclimate, and sedimentation [7]. Unlike their marine counterparts, the enrichment of elements in lacustrine oil shales is strongly influenced by the specific paleolake water chemistry, provenance characteristics, and variations in diagenetic and post-diagenetic processes [8]. Consequently, the mobilization and fixation mechanisms for trace elements, including hazardous ones such as As, Cd, Pb, and U, may exhibit significant differences.

In recent years, increasing attention has been paid to the speciation, mobility, and environmental behavior of trace elements in oil shale systems. Studies have shown that hazardous elements such as As, Mo, U, and Pb can occur in multiple forms, including organic-bound, sulfide-associated, and clay-adsorbed phases, which significantly influence their mobility during thermal processing and weathering [9–11]. Furthermore, the environmental impacts of oil shale exploitation have been widely documented, highlighting potential risks to soil and groundwater systems [12, 13]. Despite these advances, most existing studies have focused either on marine systems or on bulk geochemical characteristics, with relatively limited attention to the coupling between sedimentary environment evolution and hazardous element enrichment in continental lacustrine basins. In particular, the mechanisms linking paleoenvironmental conditions (e.g., redox state, salinity, and climate) with trace element accumulation remain insufficiently constrained.

Despite their significance, previous studies in the Lunpola Basin have primarily focused on organic matter enrichment, with limited attention to the systematic characterization of hazardous trace elements and their coupling with sedimentary environments [14]. Consequently, critical knowledge gaps remain regarding the abundance, enrichment degree, and controlling mechanisms of key toxic elements within these oil shale sequences. Furthermore, the unique

Cenozoic tectonic activity triggered by the India–Eurasia collision, coupled with the evolution of the paleolake basin, likely led to distinctive pathways for element input and specific horizons of enrichment [15]. Compounding these concerns, the Lunpola Basin sits within a high-altitude, cold, and ecologically fragile region. The potential release of hazardous elements during future development activities could significantly heighten the risk of regional environmental contamination.

Addressing these uncertainties, this study leverages comprehensive major and trace element data from a detailed profile in the Lunpori area of the Lunpola Basin. Our objectives are threefold: (1) to elucidate the vertical differentiation patterns of elements and their relationships with sedimentary environments and organic matter enrichment mechanisms; (2) to quantitatively characterize the concentration ranges and enrichment factors of representative hazardous elements (e.g., As, Mo, Pb, U), using global shale standards and upper continental crustal Clarke values to identify priority control elements [16, 17]; and (3) to explore the dominant controlling factors governing element enrichment within this continental lacustrine setting. This work aims to establish essential environmental geochemical baselines for the sustainable development of hydrocarbon resources on the Tibetan Plateau, while also contributing a crucial case study to global models of hazardous element cycling in continental oil shale systems.

2. Geological setting

The Lunpola Basin, situated in the central Tibetan Plateau, represents a significant hydrocarbon-bearing basin, the southeastern part of the Qiangtang Basin [18]. It lies within the Bangong–Nujiang Suture Zone, bordered by the Nima Basin to the west and the Bangor Basin to the south (Fig. 1a). This E–W trending basin extends linearly along the suture zone as an elongated structural depression. Developed atop the Yanshan Fold Belt, the Lunpola Basin is a Cenozoic continental rift basin [15, 19]. Paleogene strata are extensively distributed throughout the basin, with the composite stratigraphic sequence reaching a thickness of approximately 4000 m [20]. This succession comprises the lower Niubao Formation (Fm) and the upper Dingqinghu Fm. This research primarily targets the Dingqinghu Fm, which consists dominantly of Cenozoic lacustrine sediments. Key lithologies include gray mudstones and economically significant oil shale units that form the principal subject of our geochemical investigation.

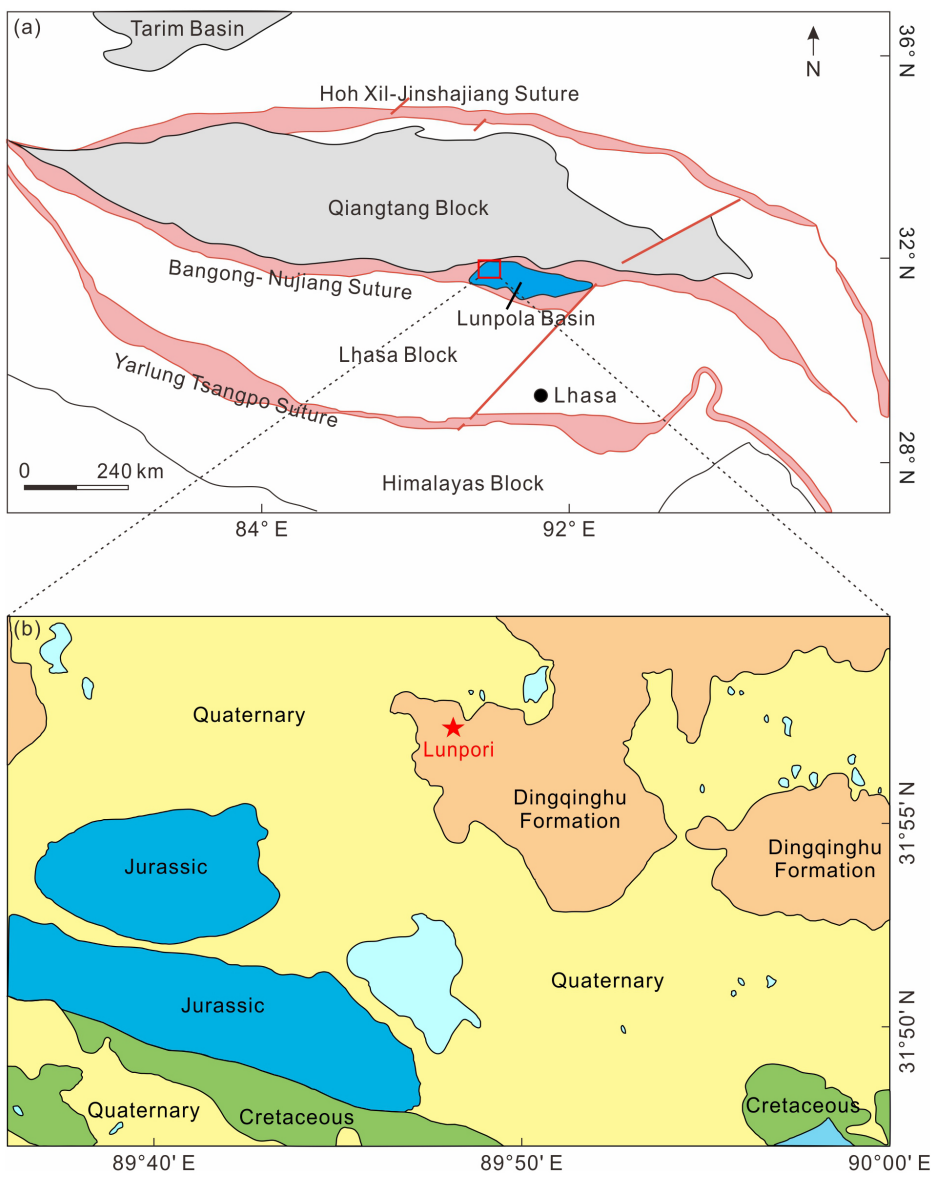


Fig. 1. Geological background: (a) simplified tectonic map of the Tibetan Plateau [21], (b) simplified geological map of the study area, with a red five-pointed star indicating the location of the Lunpori section (modified from Fu et al. 2015 [15]).

3. Samples and analytical methods

The study section is located in the Lunpori section within the Lunpola Basin, Tibet, China (Fig. 1b). The Lunpori section represents one of the most representative field outcrops for studying the Lunpola Basin on the Tibetan Plateau. Oil shale intervals were identified in the field, and samples were collected from freshly exposed rock surfaces. A total of 38 samples were collected from a 21-m-thick stratigraphic interval, comprising 23 oil shale samples and 15 mudstone samples. Immediately after collection, all samples were placed in sealed bags to minimize contamination and oxidation. Following cleaning and drying, the samples were crushed and ground to a particle size of <200 mesh.

Major element concentrations were determined by X-ray fluorescence (XRF) spectroscopy using a PW2404 spectrometer, following analytical procedures similar to those described by Kimura (1998) with minor modifications [22]. The analytical uncertainty is typically <5%. Trace element analysis for most elements (excluding As, Hg, and Se) was performed using inductively coupled plasma mass spectrometry (ICP-MS). For ICP-MS analysis, samples were digested in a microwave furnace using HF + HNO₃ (HF: HNO₃ = 1: 2). The detection limits for elements range from 0.n to $n \times 10^{-12}$ (n = 1–9). As, Hg, and Se concentrations were measured via atomic fluorescence spectrometry (AFS) using an AFS2202 instrument. The analysis of major and trace elements was carried out at the Beijing Research Institute of Uranium Geology.

Total organic carbon (TOC) and total sulfur (TS) values were determined by a LECO CS-800 carbon–sulfur analyzer. The crushed samples (200 mesh) were heated from ambient temperature to 1200 °C in an induction furnace after removing carbonate with hydrochloric acid. Analytical procedures follow Yeomans and Bremner (1989) [23].

Enrichment factors (EF) were calculated using Al as the reference element and the composition of the upper continental crust (UCC) as the background, following Rudnick and Gao (2003) [24]. The calculation results are shown in the Supplementary Table (Table S1). To evaluate the relationships between elemental concentrations and organic matter accumulation, statistical analyses were performed using IBM SPSS Statistics. Pearson correlation coefficients were employed to assess linear relationships between variables.

4. Results and discussion

4.1. Major and trace elements geochemistry

For most oil shale samples, the most abundant elements are Si, Al, and Ca. Fe, Mg, and K are subdominant, while concentrations of other major elements (Na, Ti, P, Mn) are consistently below 1.0% (Table 1).

Table 1. Concentrations of TOC, total sulfur, and major elements in samples from the Lunpola oil shale, %

Sample	Lithology	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₅	MnO	TOC	TS
LPR-38	Mudstone	24.12	7.19	1.15	0.91	31.57	2.75	1.71	0.62	0.32	0.120	0.073	0.62	0.42
LPR-37	Mudstone	24.74	7.31	0.94	1.12	31.65	2.27	1.73	0.68	0.33	0.180	0.067	0.71	0.51
LPR-36	Mudstone	26.43	7.90	1.42	1.27	28.71	3.21	1.85	0.65	0.36	0.330	0.068	0.94	0.56
LPR-35	Mudstone	25.00	7.73	2.08	1.23	28.92	3.24	1.74	0.62	0.34	0.320	0.081	0.93	0.58
LPR-34	Mudstone	27.01	8.15	2.34	0.86	27.70	3.37	1.90	0.76	0.37	0.320	0.082	0.95	0.43
LPR-33	Mudstone	31.01	9.40	2.95	0.59	24.19	3.51	2.19	0.82	0.41	0.230	0.077	0.98	0.29
LPR-32	Mudstone	36.04	11.49	3.20	1.09	19.13	3.34	2.64	0.78	0.46	0.190	0.076	0.21	0.75
LPR-31	Oil shale	38.95	13.86	3.24	1.68	7.19	3.04	2.97	1.00	0.47	0.370	0.065	12.42	0.89
LPR-30	Oil shale	40.20	14.09	3.31	1.65	6.72	2.80	3.05	1.06	0.50	0.460	0.057	14.38	0.85
LPR-29	Oil shale	47.08	17.78	3.00	1.56	2.90	2.64	3.41	1.52	0.60	0.080	0.049	7.35	0.79
LPR-28	Oil shale	49.11	18.16	3.32	1.17	2.09	2.56	3.56	1.28	0.64	0.094	0.045	7.24	0.68
LPR-27	Oil shale	47.97	17.23	3.50	1.90	3.88	2.57	3.53	1.21	0.60	0.100	0.057	8.28	0.93
LPR-26	Oil shale	46.77	16.36	3.39	1.64	4.36	2.70	3.36	1.46	0.59	0.120	0.052	9.94	0.84
LPR-25	Oil shale	45.38	16.04	3.69	1.30	2.64	2.71	3.13	1.14	0.56	0.140	0.060	10.89	0.81
LPR-24	Oil shale	41.71	14.40	2.71	2.08	4.43	3.00	2.95	1.08	0.52	0.150	0.052	11.78	0.91
LPR-23	Oil shale	47.08	16.32	4.42	1.60	2.48	2.66	3.13	1.30	0.57	0.090	0.035	9.42	0.74
LPR-22	Oil shale	46.37	15.56	4.69	1.21	3.77	2.82	3.07	1.16	0.55	0.110	0.048	10.69	0.68
LPR-21	Oil shale	49.39	15.79	4.03	1.09	4.24	2.57	3.25	0.95	0.59	0.170	0.038	11.72	0.62
LPR-20	Oil shale	44.21	14.79	3.61	1.08	5.87	2.76	2.98	1.56	0.51	0.700	0.046	16.38	0.56

Continued on the next page

Table 1. Continued

Sample	Lithology	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	CaO	MgO	K ₂ O	Na ₂ O	TiO ₂	P ₂ O ₃	MnO	TOC	TS
LPR-19	Oil shale	48.74	16.62	3.88	0.84	2.92	2.68	3.23	1.53	0.58	0.460	0.034	14.65	0.64
LPR-18	Oil shale	40.97	14.00	3.41	1.74	7.20	3.02	2.74	1.37	0.46	0.860	0.058	17.28	0.86
LPR-17	Oil shale	41.14	15.53	3.02	1.90	4.18	2.53	2.93	0.91	0.51	0.700	0.044	16.75	0.87
LPR-16	Oil shale	43.69	16.26	1.96	3.02	3.19	2.55	3.07	1.00	0.53	0.470	0.036	14.94	1.43
LPR-15	Oil shale	39.53	14.38	2.99	2.00	4.49	3.67	2.84	0.88	0.46	0.180	0.073	11.37	0.98
LPR-14	Oil shale	41.83	15.58	4.08	1.13	5.33	3.90	3.04	0.78	0.49	0.150	0.085	10.27	0.76
LPR-13	Oil shale	36.91	13.32	4.44	0.96	11.56	5.37	2.71	1.11	0.43	0.130	0.065	8.74	0.74
LPR-12	Oil shale	36.30	13.04	2.95	1.75	10.55	4.87	2.64	1.05	0.41	0.130	0.059	7.68	0.92
LPR-11	Oil shale	47.97	18.12	4.28	1.29	3.01	2.56	3.74	0.64	0.58	0.230	0.048	13.46	0.58
LPR-10	Oil shale	46.77	17.67	4.94	1.05	2.74	2.47	3.65	1.35	0.56	0.260	0.042	13.25	0.79
LPR-9	Oil shale	47.24	18.10	4.38	1.28	2.70	2.44	3.70	1.46	0.58	0.170	0.032	11.51	0.78
LPR-8	Mudstone	50.24	17.13	4.81	1.48	6.22	2.69	3.60	1.24	0.64	0.089	0.079	2.45	0.48
LPR-7	Mudstone	53.01	16.46	4.94	1.06	5.46	2.51	3.41	1.35	0.66	0.088	0.074	2.69	0.56
LPR-6	Mudstone	54.72	16.41	4.42	1.42	5.12	2.40	3.36	1.24	0.69	0.088	0.072	2.43	0.64
LPR-5	Mudstone	57.94	15.36	4.48	1.19	4.53	2.09	3.14	1.29	0.70	0.086	0.063	2.77	0.58
LPR-4	Mudstone	58.54	15.03	4.61	0.87	4.75	2.07	3.06	1.25	0.68	0.091	0.067	1.06	0.43
LPR-3	Mudstone	57.40	15.17	4.48	0.95	5.19	2.10	3.11	1.24	0.68	0.087	0.076	1.02	0.48
LPR-2	Mudstone	59.21	14.67	4.51	0.95	4.81	2.01	3.00	1.17	0.66	0.093	0.064	1.09	0.47
LPR-1	Mudstone	55.64	15.76	4.63	0.94	5.54	2.25	3.24	1.15	0.68	0.097	0.073	1.05	0.45

In the oil shales of the Lunpola Basin, Tibet, the most enriched trace elements relative to Clarke values [8] are B ($46\times$) and As ($45\times$), followed by Cs ($10\times$), Li ($5.4\times$), Mo ($5.2\times$), Bi ($5.1\times$), Pb ($3.8\times$), U ($3.3\times$), Hg ($2.9\times$), Yb ($2.8\times$), Th ($2.1\times$), and Sn ($2.0\times$). Other elements exhibit concentrations slightly above or below the corresponding global averages. Compared to Australian oil shale samples reported by Patterson et al. (1986) [17], Lunpola oil shales are enriched in Be, Sc, Ga, Rb, Zr, Nb, Sn, Cs, Ce, Pr, Nd, Hf, Pb, and Th. Conversely, V, Cu, Zn, Se, Mo, Cd, and U show lower concentrations. Elements including F, Cr, Co, Ni, As, Sr, Y, Ba, La, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and Bi have concentrations similar to those in Australian Julia Creek oil shales (Table 2).

Vertically, most trace elements are enriched in the oil shale interval compared to the overlying and underlying mudstone sections, displaying a downward-decreasing, then upward-increasing trend. The elements Zn, Rb, Zr, Sn, REEs, Hf, and Th show continuous upward enrichment, while Sr exhibits persistent depletion. Ba content decreases within the oil shale unit, demonstrating an initial increase followed by a vertical decrease.

4.2. Sedimentary environment

Analyzing the depositional environment of oil shales is crucial for understanding trace element enrichment mechanisms [25, 26]. Such enrichment primarily depends on source supply, physicochemical properties of element migration, and synergistic effects of geological processes and elemental characteristics [15, 27, 28]. These trace elements occur mainly as independent minerals, adsorbed on clay minerals, bound to organic matter, or associated with other minerals [29]. Therefore, sedimentary environment analysis aids in deciphering trace element enrichment mechanisms.

4.2.1. Paleosalinity

Paleosalinity of depositional water bodies is vital for reconstructing paleoenvironmental evolution and trace element enrichment. Trace element distribution patterns under varying salinity conditions make them valuable inorganic geochemical proxies for paleosalinity reconstruction. Currently, B content and Sr/Ba ratios are widely applied paleosalinity indicators. Higher water salinity correlates with increased B adsorption in sediments [30]. Typically, seawater contains 80–125 $\mu\text{g/g}$ B, while freshwater environments have <60 $\mu\text{g/g}$ B [30].

Sr and Ba exhibit relatively similar chemical properties. In the same sedimentary environment, due to Sr's higher migration capacity compared to Ba, when the mineralization of the aqueous medium is very low (indicating low salinity), both Sr and Ba occur in the form of bicarbonates [31]. As salinity increases, Ba precipitates first as BaSO_4 , leaving Sr enriched in water. At higher salinities, Sr increasingly precipitates as SrSO_4 [31]. Generally,

Table 2. Concentrations of trace elements in samples from the Lunpola oil shale, µg/g

Sample	Li	B	V	Cr	Ni	Cu	As	Rb	Sr	Mo	Sn	Cs	Yb	Hg	Pb	Bi	Th	U
LPR-38	47.9	175	64.6	63.9	48.4	26.0	8.29	65.6	288	1.02	1.66	13.0	1.50	0.23	17.9	0.42	10.5	4.35
LPR-37	45.6	163	63.0	68.9	51.6	26.6	11.4	65.9	313	1.40	1.85	12.5	1.57	0.20	17.8	0.33	10.9	4.51
LPR-36	47.6	192	65.6	71.5	73.9	29.9	18.4	71.3	498	2.08	1.32	12.6	1.67	0.23	19.0	0.28	11.2	4.63
LPR-35	48.6	196	71.2	73.2	91.4	28.0	19.0	69.9	552	3.04	1.78	12.8	1.72	0.17	18.6	0.16	11.8	5.08
LPR-34	50.6	179	71.4	73.9	83.8	27.3	17.8	75.5	555	2.33	1.84	12.6	1.71	0.15	17.6	0.35	11.8	4.92
LPR-33	56.8	200	76.8	82.7	85.5	28.8	17.0	87.2	523	2.23	2.05	14.2	1.80	0.14	20.6	0.35	13.8	4.84
LPR-32	69.2	291	89.5	100.0	86.8	31.4	24.3	110.0	459	2.61	2.55	19.2	1.90	0.19	24.0	0.49	14.2	5.34
LPR-31	87.6	418	113	94.8	114.0	61.3	128	134.0	298	10.20	3.65	29.1	2.23	0.31	58.0	1.00	19.2	8.18
LPR-30	94.0	443	117	99.9	118.0	64.3	105	136.0	291	9.56	3.82	30.0	2.46	0.26	60.1	0.93	20.8	9.91
LPR-29	113.0	544	115	97.8	70.6	36.6	71.0	173.0	188	4.38	4.78	36.8	2.84	0.24	42.4	0.71	22.6	6.01
LPR-28	108.0	519	111	100.0	69.6	40.5	76.6	177.0	166	2.86	4.61	35.6	2.86	0.27	42.3	0.71	23.0	6.12
LPR-27	117.0	550	131	99.6	83.1	43.9	59.0	169.0	194	4.01	4.59	38.4	2.72	0.13	57.7	0.84	21.6	6.77
LPR-26	123.0	513	127	100.0	81.7	45.9	68.0	158.0	201	4.82	4.61	36.9	2.84	0.14	59.2	0.86	21.0	7.46
LPR-25	102.0	446	122	100.0	166.0	63.4	74.5	159.0	166	10.30	4.24	33.8	2.60	0.18	53.4	0.92	20.2	8.13
LPR-24	99.3	429	125	112.0	133.0	65.0	57.9	140.0	195	13.40	3.92	29.1	2.42	0.21	46.9	0.84	18.5	9.12
LPR-23	126.0	419	104	89.4	83.0	46.2	57.9	164.0	155	6.88	4.23	30.2	2.51	0.24	49.3	0.89	20.4	6.19
LPR-22	122.0	387	106	93.9	80.1	41.6	98.2	155.0	186	7.35	4.11	29.7	2.56	0.17	49.7	0.76	19.8	7.62
LPR-21	156.0	475	117	94.8	83.2	33.6	43.4	161.0	180	3.14	4.55	34.7	2.63	0.21	42.6	0.80	20.7	6.71
LPR-20	131.0	459	100	87.1	89.4	40.1	96.8	148.0	273	4.98	3.56	27.3	2.24	0.25	37.8	0.75	17.6	10.3
LPR-19	204.0	488	114	89.8	89.0	38.6	93.2	168.0	196	3.24	4.34	27.6	2.81	0.23	44.5	0.84	22.1	11.8

Continued on the next page

Table 2. Continued

Sample	Li	B	V	Cr	Ni	Cu	As	Rb	Sr	Mo	Sn	Cs	Yb	Hg	Pb	Bi	Th	U
LPR-18	129.0	447	100	79.5	95.0	45.8	98.4	137.0	337	8.58	3.38	26.7	2.23	0.25	41.0	0.80	17.5	13.5
LPR-17	101.0	452	128	104.0	106.0	59.3	83.5	147.0	246	9.49	4.21	33.5	2.95	0.31	52.8	0.95	22.8	18.6
LPR-16	99.8	475	123	99.8	95.7	55.5	128	156.0	205	10.60	4.27	34.2	2.94	0.35	49.6	0.94	21.0	14
LPR-15	81.8	448	104	97.4	144.0	71.0	103	137.0	204	22.20	3.52	28.0	2.40	0.32	50.4	1.09	17.8	8.6
LPR-14	85.8	436	117	100.0	138.0	65.4	97.9	144.0	213	22.80	4.00	31.2	2.59	0.28	49.1	1.01	19.7	8.39
LPR-13	60.6	350	80.4	81.1	72.4	49.5	31.1	126.0	370	8.02	2.75	21.5	1.69	0.20	40.7	0.98	12.9	4.69
LPR-12	81.4	336	107	82.1	67.4	42.1	51.1	124.0	386	9.55	3.72	28.8	2.18	0.30	45.6	0.86	17.0	6.39
LPR-11	94.3	512	133	102.0	72.7	45.7	62.8	185.0	166	3.11	4.69	38.1	2.70	0.19	47.6	1.01	22.9	8.49
LPR-10	91.6	581	119	98.8	71.0	48.3	71.4	181.0	166	3.41	4.14	33.3	2.48	0.19	44.2	0.95	20.8	10.2
LPR-9	132.0	604	131	98.4	65.6	46.0	55.6	184.0	150	3.09	4.46	29.6	2.66	0.18	44.0	0.92	21.8	9.84
LPR-8	88.1	451	109	89.6	71.7	26.1	10.4	176.0	210	1.39	4.66	36.0	2.71	0.12	35.8	0.72	23.0	4.57
LPR-7	78.5	412	100	92.9	67.7	25.4	12.4	167.0	203	1.42	4.48	33.0	2.59	0.14	33.6	0.67	22.6	4.14
LPR-6	80.8	398	99.4	92.5	66.9	25.6	12.2	165.0	189	1.85	4.47	32.9	2.62	0.14	34.1	0.67	22.7	4.09
LPR-5	72.2	348	86.4	83.8	63.0	23.0	12.7	155.0	170	1.40	4.08	28.6	2.48	0.14	31.4	0.72	21.8	3.8
LPR-4	66.6	311	81.1	86.7	61.0	21.9	13.5	150.0	177	1.06	3.89	26.4	2.27	0.13	28.4	0.52	19.8	3.39
LPR-3	70.9	335	84.4	93.4	63.5	22.5	13.5	152.0	183	1.04	4.06	27.6	2.35	0.11	28.6	0.55	20.3	3.64
LPR-2	68.4	310	86.1	90.3	58.3	21.6	15.1	145.0	183	1.27	4.06	27.4	2.48	0.13	30.9	0.53	22.1	3.9
LPR-1	62.7	374	82.1	95.3	63.2	22.6	12.9	157.0	196	0.89	3.83	26.4	2.25	0.13	28.9	0.61	19.4	3.63
Clarke value ¹	20	10	135	100	75	55	1.7	90	375	1.5	2.0	3.0	0.9	0.08	13	0.17	9.6	2.7
Australian oil shale ²	-	-	2000	98	160	110	50.0	22	400	270	1.0	2.2	3.0		6	1.00	2.3	30

¹ Taylor, 1964 [16]; ² Patterson et al. 1986 [17].

$\text{Sr}/\text{Ba} > 0.5$ indicates saline water, 0.2–0.5 suggests brackish water, and < 0.2 implies freshwater.

In the oil shale of the Lunpola Basin, the B content ranges from 291 to 604 $\mu\text{g}/\text{g}$, with a mean value of 459.3 $\mu\text{g}/\text{g}$. The Sr/Ba ratio varies between 0.37 and 0.98, averaging 0.62, indicating an overall brackish to saline lacustrine depositional environment with elevated salinity (Fig. 2).

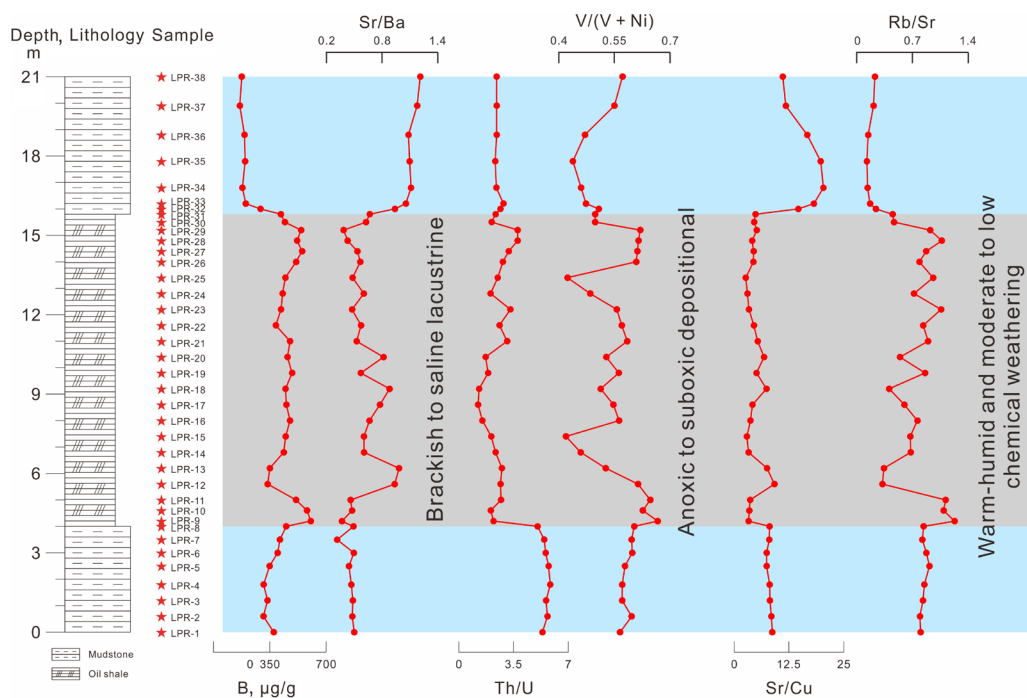


Fig. 2. Sedimentary environment analysis of Lunpola oil shales.

4.2.2. Redox conditions

In oxic waters, U occurs as soluble U^{6+} , leading to sedimentary depletion. Under reducing conditions, insoluble U^{4+} causes enrichment. Th exists as insoluble Th^{4+} and is redox-insensitive [32]. Conventionally, $\text{Th}/\text{U} < 2$ indicates anoxia, 2–7 implies suboxia, and > 7 denotes oxic conditions [33]. $\text{V}/(\text{V} + \text{Ni})$ is another key redox proxy. In oxic marine settings, Ni occurs as soluble Ni^{2+} , NiCl^+ , NiCO_3 , or humate complexes. Under moderate reduction (without H_2S), Ni is released from organic complexes [34]. In strongly reducing H_2S -rich environments, Ni forms insoluble NiS and incorporates into pyrite [35]. V enriches more readily than Ni under anoxia. $\text{V}/(\text{V} + \text{Ni}) > 0.54$ indicates anoxia, 0.46–0.54 suggests suboxia, and < 0.46 reflects oxic conditions.

In Lunpola oil shales, Th/U ratios range from 1.22 to 3.76 (avg. 2.4), and V/(V + Ni) ranges from 0.42 to 0.67 (avg. 0.55), indicating predominantly anoxic to suboxic depositional waters (Fig. 2).

The positive correlations between redox-sensitive trace elements and total sulfur (TS) suggest a potential association with sulfide phases. Similarly, the correlation between certain elements and Al_2O_3 indicates a possible affinity with clay minerals [36–38]. However, these interpretations are based on indirect geochemical evidence rather than direct mineralogical observations. Therefore, the inferred occurrence modes should be treated with caution. Despite this limitation, such proxy-based approaches have been widely used in previous studies to infer element associations in sedimentary systems.

4.2.3. Paleoclimate

Sr is a typical aridity-favoring element, enriching in arid-climate sediments. Low Sr indicates humid climates, while high Sr reflects aridity. Cu enriches under humid conditions; thus, warmer/drier climates increase Sr/Cu ratios. Typically, Sr/Cu = 1.3–5 indicates warm–humid climates, 5–10 implies semi-humid/semi-arid conditions, and > 10 suggests hot-arid climates [39].

Rb and Sr undergo significant fractionation due to contrasting chemical behaviors. Rb-bearing minerals are weathering-resistant, and Rb adsorbs readily onto clays. Sr-bearing minerals weather easily and are leached by water [40, 41]. Rb/Sr > 1 reflects high chemical weathering intensity, while < 1 indicates moderate to low weathering.

In Lunpola oil shales, Sr/Cu ratios (excluding an anomalous value of 14.6 at the mudstone contact) range from 2.61 to 9.17 (avg. 4.62), suggesting overall warm–humid conditions. Rb/Sr ratios range from 0.24 to 1.23 (avg. 0.74), indicating moderate to low chemical weathering intensity (Fig. 2).

4.2.4. Organic matter enrichment setting

Lunpola oil shales were deposited in a brackish to saline lacustrine basin. Elevated salinity reduced microbial activity, limiting organic matter consumption in degradation chains and enhancing preservation of primary productivity. The moderate P_2O_5 –TOC correlation (Pearson's $r = 0.59$, $p < 0.01$; Fig. 4j) implies limited productivity control on organic enrichment, likely due to high-salinity stress on biota.

Salinity gradients induced strong water stratification, inhibiting vertical mixing. Bottom waters became anoxic/sulfidic via oxygen consumption from organic degradation, creating optimal preservation conditions [42–44]. Concurrent warm–humid climates with moderate to low chemical weathering limited terrigenous input. This promoted aquatic productivity (e.g., diatoms, cyanobacteria), lake expansion, and photosynthesis, while reducing organic matter dilution by clastics [15, 45]. However, weak weathering restricted

nutrient inputs (P, Fe, Si), potentially limiting productivity. Thus, climate/weathering exerted moderate control on organic enrichment, whereas clastic input and productivity were secondary. The primary enrichment drivers were exceptional preservation under high salinity and anoxia (Fig. 2).

4.3. Potentially hazardous trace elements in oil shale seams

The enrichment of hazardous trace elements in the Lunpola oil shales can be interpreted as a result of coupled biogeochemical processes. Under anoxic to suboxic conditions, redox-sensitive elements such as U and Mo are reduced to insoluble forms and precipitate within sediments. Simultaneously, elevated salinity promotes water column stratification, limiting oxygen replenishment and enhancing bottom-water anoxia. Organic matter provides additional binding sites through complexation and adsorption, while sulfide formation further immobilizes elements via incorporation into metal sulfides. This multi-factor coupling mechanism explains the strong association between TOC, TS, and trace element enrichment observed in this study.

Most hazardous elements in Lunpola oil shales show significant positive correlations with TOC. Key enriched hazardous elements are As ($45\times$ Clarke value), Mo ($5.2\times$), Pb ($3.8\times$), and U ($3.3\times$) (Fig. 3). EF values confirm that As shows strong enrichment, while Mo, Pb, and U exhibit moderate enrichment, consistent with the enrichment patterns inferred from Clarke-normalized ratios. Their high toxicity requires careful management during exploitation to mitigate human/environmental risks.

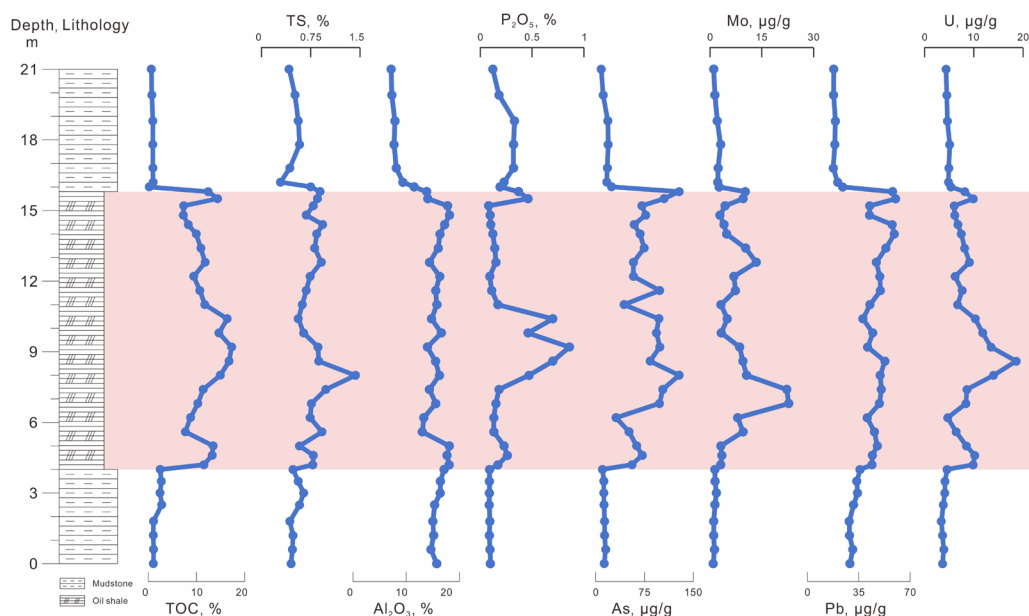


Fig. 3. Vertical variations of selected elements in the Lunpola oil shale section.

4.3.1. Arsenic

Arsenic concentrations range from 24.3 to 128 $\mu\text{g/g}$ (avg. 76.5 $\mu\text{g/g}$), vastly exceeding the Clarke value (1.7 $\mu\text{g/g}$), making it the most enriched hazardous element. Given the acute toxicity of As compounds, arsenic poses the highest potential hazard (Fu et al. 2012). As is conventionally ascribed to organic binding or sulfide mineral association [46, 47]. Figure 3 shows strong As–TOC (Pearson's $r = 0.88$, $p < 0.01$; Fig. 4a) and As–TS (Pearson's $r = 0.73$, $p < 0.01$; Fig. 4e) correlations, indicating dual organic/sulfide affinity (organic > sulfide). This affinity – amplified by high TOC and sulfides under suboxia – drives As enrichment during deposition.

4.3.2. Molybdenum

Though not classified as a hazardous air pollutant, Mo exhibits documented environmental risks [47]. Mo concentrations range from 2.61 to 22.8 $\mu\text{g/g}$ (avg. 7.86 $\mu\text{g/g}$) in Lunpola, exceeding the Clarke value (1.5 $\mu\text{g/g}$). Similar to As, Mo associates with organic matter and sulfides, showing significant Mo–TOC (Pearson's $r = 0.55$, $p < 0.01$; Fig. 4b) and Mo–TS (Pearson's $r = 0.63$, $p < 0.01$; Fig. 4f) correlations (stronger for TS). This implies redox-controlled enrichment via organic/sulfide pathways. As a redox-sensitive element, Mo occurs predominantly as insoluble Mo^{4+} in the anoxic to suboxic depositional waters of the Lunpola Basin [34].

4.3.3. Lead

Pb poses severe risks to both human health and the environment, and is recognized as a common heavy metal contaminant. In the Lunpola Basin oil shales of Tibet, Pb concentrations range from 24 to 60.1 $\mu\text{g/g}$ (avg. 47.2 $\mu\text{g/g}$), exceeding the Clarke value (13 $\mu\text{g/g}$). Pb exhibits strong positive correlations with organic matter (Pearson's $r = 0.80$, $p < 0.01$; Fig. 4c) and total sulfur (Pearson's $r = 0.72$, $p < 0.01$; Fig. 4g), indicating that its enrichment is primarily controlled by organic material and sulfides. Additionally, a significant correlation exists between Pb and Al_2O_3 (Pearson's $r = 0.69$, $p < 0.01$; Fig. 4k), attributable to Pb adsorption onto clay minerals, suggesting that clay content also contributes to Pb accumulation.

4.3.4. Uranium

U is the heaviest primordial element, posing chemical and radiological hazards. U concentrations range from 4.69 to 18.6 $\mu\text{g/g}$ (avg. 8.85 $\mu\text{g/g}$) in Lunpola, exceeding the Clarke value (2.7 $\mu\text{g/g}$). Strong U–TOC (Pearson's $r = 0.87$, $p < 0.01$; Fig. 4d) and U–TS (Pearson's $r = 0.64$, $p < 0.01$; Fig. 4h) correlations reflect redox-controlled organic/sulfide enrichment. As a key redox proxy, U is deposited as insoluble U^{4+} in anoxic to suboxic waters [48]. The U– P_2O_5 correlation (Pearson's $r = 0.75$, $p < 0.01$; Fig. 4i) also implies a productivity influence on U enrichment. Therefore, the redox conditions and productivity during the deposition of oil shale exerted a critical influence on U enrichment [49].

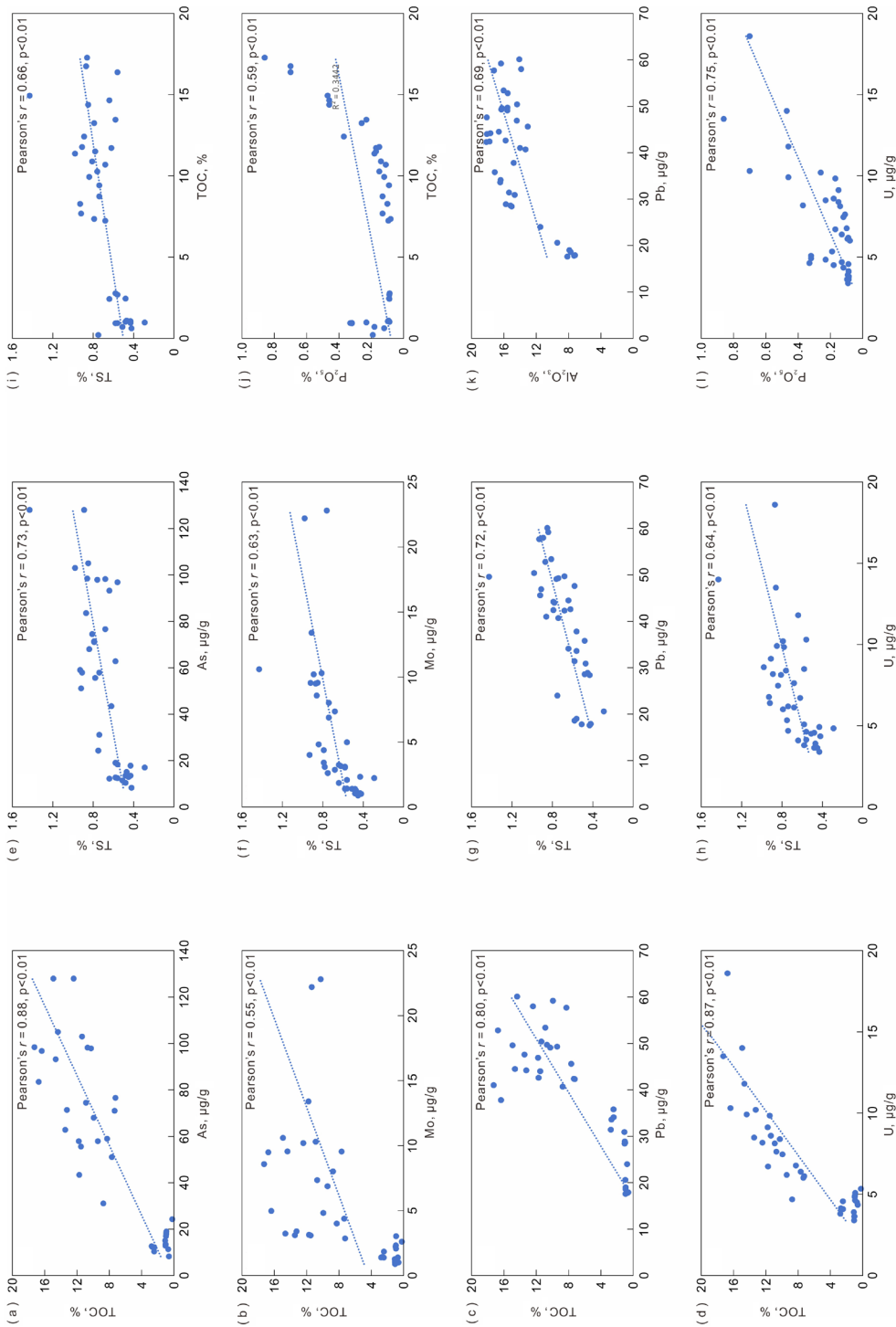


Fig. 4. Relationship between potentially hazardous trace elements and some other elements.

5. Conclusions

1. In the oil shales of the Lunpola Basin, Tibet, the most enriched trace elements relative to Clarke values (Taylor 1964) are B (46×) and As (45×), followed by Cs (10×), Li (5.4×), Mo (5.2×), Bi (5.1×), Pb (3.8×), U (3.3×), Hg (2.9×), Yb (2.8×), Th (2.1×), and Sn (2.0×) relative to global averages. Other elements exhibit concentrations marginally above or below their respective global mean values. Moreover, compared to overlying and underlying mudstone intervals, most trace elements are significantly enriched within the oil shale unit.
2. The Lunpola oil shales were deposited in a brackish to saline lacustrine basin with elevated salinity, under predominantly anoxic to suboxic water conditions, and in a warm–humid paleoclimate characterized by moderate to low chemical weathering intensity.
3. The enrichment of hazardous elements is primarily controlled by redox conditions and organic matter accumulation, with additional contributions from sulfide formation and clay mineral adsorption.
4. This study demonstrates that the coupling between depositional environment and organic matter preservation plays a key role in controlling hazardous element enrichment in continental oil shale systems, providing important implications for both paleoenvironmental reconstruction and environmental risk assessment during resource exploitation.

Data availability statement

The data supporting the findings of this study are available within the article.

Acknowledgments

This research was supported by Oil & Gas Major Project (No. 2025ZD1400700). The publication costs of this article were partially covered by the Estonian Academy of Sciences.

Supplementary online data

Supplementary online data to this article can be found at <https://doi.org/10.3176/oil.2026.4.S03> and includes Table S1: Al-normalized enrichment factors of As, Mo, Pb, and U in Lunpola oil shales (UCC reference).

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[BMIM]BF₄ and [BMIM]PF₆ ionic liquids for sulfur extraction from Jordanian shale oils

Rasha A. Hajarat^{(a)*}, Omar S. Al-Ayed^{(b)*}, Mohammed Matoq^(b)

^(a) Department of Chemical Engineering, Mutah University, Karak 61710, Jordan

^(b) Department of Chemical Engineering, Faculty of Engineering Technology, Amman Marka 11134, Al-Balqa Applied University, Jordan

Received 8 May 2026, accepted 21 October 2026, available online 23 October 2026

Abstract. Two different shale oils were produced by the pyrolysis of oil shale from the Attarat Um-Ghudran and El-Lajjun areas in Jordan. The ionic liquids [BMIM]BF₄ and [BMIM]PF₆ were used to extract sulfur compounds from the shale oils. The two shale oils generated from Attarat and El-Lajjun were found to contain 12.1 and 11.2 wt.% sulfur, respectively. The extraction of sulfur compounds from shale oil was studied at 20, 40, and 60 °C, with 40 °C being the optimum. The volume ratios of ionic liquid to shale oil (IL/SO) investigated were 1.0:1.0, 1.0:3.0, 1.0:5.0, 1.0:8.0, and 1.0:10.0. For Attarat shale oil, the 1.0:5.0 ratio resulted in removal efficiencies of 58.7% (7.1/12.1) and 54.6% (6.6/12.1) for [BMIM]PF₆ and [BMIM]BF₄, respectively, which were lower than those calculated for the 1.0:1.0 (IL/SO) ratio, i.e., 62.8% (7.6/12.1) and 57.9% (7.0/12.1), respectively. However, the 1.0:5.0 ratio is more economical and was therefore selected. Based on the calculated extraction efficiencies, [BMIM]PF₆ is a slightly more effective extracting agent.

Keywords: shale oil, ionic liquids, sulfur extraction, IL/SO volume ratio.

1. Introduction

Global crude oil consumption in 2025 was estimated at 105 million barrels per day [1]. Crude oils contain between 0.2 and 5 wt.% sulfur. Assuming an average sulfur content of 2.6 wt.%, this corresponds to 2.73 million barrels of sulfur per day. If the average density of solid sulfur is assumed to be 2000 kg/m³, this would correspond to 0.868 million metric tons of sulfur, potentially producing 1.73 million metric tons of SO₂ emissions per annum. During combustion, sulfur is converted to SO₂ gas, which is a major air pollutant that contributes to acid rain. The large amount of sulfur contained in crude oil is therefore an alarming concern in terms of air pollution. Sulfur can be removed from

* Corresponding authors, hajarat@mutah.edu.jo, omar.alayed@bau.edu.jo

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crude oil using industrial treatment methods, such as hydrodesulfurization (HDS) and other processes. The sulfur removed as a byproduct can be used in the fertilizer industry to alleviate its environmental impact. Fertilizers and specialty chemicals are among the end products derived from the recovered sulfur compounds or elemental sulfur.

Oil shale resources are more than five times as abundant as crude oil resources. Oil shale can be pyrolyzed (retorted) to produce liquid shale oil. Estonia, China, and Brazil are the only countries that use shale oil produced by different commercial retorting processes [2]. Shale oils produced experimentally by pyrolysis in various laboratories in Jordan have been found to contain more than 10 wt.% sulfur [3–7]. The sulfur content of shale oils must be reduced through hydrodesulfurization or other sulfur-removal processes to less than 6 wt.%, approaching the sulfur content of crude oil [8, 33]. Accordingly, desulfurized shale oil could potentially be processed in existing crude oil refineries if its sulfur content were reduced to permissible levels for crude oil.

Sulfur compounds in shale oil range from thiols, sulfides, and disulfides, including compounds such as $\text{CH}_3\text{-S}$, $\text{CH}_3\text{-S-CH}_3$, and $\text{CH}_3\text{-S-S-CH}_3$ [9–11]. Thiols are also commonly referred to as mercaptans. Thiophenes are another class of sulfur compounds, with many derivatives such as benzothiophenes and dibenzothiophene.

The generated shale oils contain hydrocarbons in addition to the undesirable organosulfur compounds that contain sulfur, nitrogen, and oxygen atoms. One of the major disadvantages associated with shale oil production is the formation of organosulfur compounds together with the desired hydrocarbons. These sulfur-containing hydrocarbons will ultimately become a source of pollution. The average shale oil yield obtained from Jordanian oil shale from the El-Lajjun area at different pyrolysis temperatures was relatively constant at 12 wt.% [3]. In a separate study of Jordanian oil shale, sulfur contents of 9.3 and 10.5 wt.% were reported in Attarat and Sultani shale oils, respectively [4, 12]. The sulfur content in shale oil was also studied as a function of particle diameter. Investigators reported sulfur contents of 11.76, 9.93, and 8.76 wt.% for particle diameters of 2.8, 6.7, and 13.2 mm, respectively [5]. Sulfur contents ranging from 0.3 to 1.5 wt.% have been reported for kukersite shale oil [8]. Shale oils generated from the Beipiao and Fushun regions in China were found to contain 1.32 and 0.54 wt.% sulfur, respectively [13, 14]. Shale oil samples from the Oil Shale Industrialization Unit (SIX), located in São Mateus do Sul, Paraná, Brazil, were reported to contain 1.3 wt.% sulfur [15].

In general, ionic liquids (ILs) are organic salts with melting points below 100 °C and consist of organic cations and organic or inorganic anions. Properties of ILs such as nonvolatility, the ability to dissolve both organic and inorganic compounds, chemical stability, nonflammability, good thermal stability, recyclability, environmental friendliness, and high decomposition temperatures make them suitable extractants for sulfur compounds [16].

One of the recent unconventional methods for removing sulfur compounds from crude oils or their derivatives is the use of ILs. In the present study, two types of ILs were selected for extracting sulfur compounds from Jordanian Attarat Um Al-Ghudran (Attarat) and El-Lajjun shale oils. These ILs were 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆) and 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF₄). These ILs were used specifically to extract organosulfur compounds from shale oil produced by pyrolysis. [BMIM]PF₆ and [BMIM]BF₄ have been used by other investigators to extract model sulfur components from typical gasoline and diesel fuels [17]. The model components were thiophene, methylthiophene, isobutyl thiol, toluene, trimethylbenzene, hexene, 2-methylpentane, and methylcyclopentane. The ionic liquid-to-fuel molar ratios were 1:3.5 for [BMIM]PF₆ and 1:2.2 for [BMIM]BF₄, as measured by nuclear magnetic resonance (NMR) analysis. The extraction was performed at room temperature, and the results showed the highest removal of thiophene with [BMIM]PF₆, followed by [BMIM]BF₄. [BMIM]PF₆ and [BMIM]BF₄ were able to remove 3.5 and 2.5 mol of thiophene per mol of ionic liquid, respectively. The order of absorption of sulfur compounds was thiophene > methylthiophene > isobutyl thiol (butyl mercaptan). In a recent study, [BMIM]PF₆ and [BMIM]BF₄ were used to remove dibenzyl disulfide from transformer oils, and [BMIM]PF₆ was found to reduce the sulfur content of transformer oil more effectively than [BMIM]BF₄ [18]. A group of researchers used [BMIM]BF₄ with a factorial design method to extract sulfur from a mixture of different gasoline grades obtained from the local market [19]. The best extraction conditions for a 40% removal efficiency were a temperature of 35 °C, a 1:1 ionic liquid-to-feed (IL/gasoline) mass ratio, and three extraction stages. In another study, the removal efficiency of dibenzothiophene from model n-dodecane oil was 73.02% at a temperature of 30 °C and an IL/feed mass ratio of 1:1, and [BMIM]BF₄ was recycled four times without loss of activity [20]. Heavy Iraqi crude oil containing 3.79 wt.% sulfur was tested for sulfur extraction using [BMIM]BF₄ [21]. The results indicated a 37% removal efficiency after a single stage extraction at a temperature of 35 °C and an IL/crude oil mass ratio of 1:3. It is evident from the cited literature that the ILs selected for this study are capable of extracting sulfur compounds from model oils, gasoline, and crude oils. The selection of these ILs for the present study was based on these findings.

The main objective of the present work was to test the ability of the ILs [BMIM]PF₆ and [BMIM]BF₄ to extract sulfur compounds from Attarat and El-Lajjun shale oils generated by pyrolysis. The novelty of the present work lies in the successful reduction of the sulfur content of high-sulfur Jordanian shale oils, containing approximately 10–12 wt.% sulfur, to levels comparable to those of conventional crude oils. The successful removal was evaluated by investigating the effects of extraction temperature and the IL/SO volume ratio on sulfur removal efficiency. The extraction efficiency was calculated

based on the mass of sulfur measured as a weight percentage in the shale oils investigated.

2. Materials and methods

2.1. Oil shale samples

One of the oil shale samples was obtained from the project site of Attarat Power Company in Jordan, and the other sample was collected from the El-Lajjun area. The Attarat Power Plant is located on a 37 km² development site in a remote, uninhabited area of Attarat Um Al-Ghudran (31°16'08" N, 36°26'52" E), 110 km southeast of Amman, the capital of Jordan, and 40 km east of the village of Al-Qatrana, along the desert highway to Aqaba. The El-Lajjun region is located 25 km west of Al-Qatrana, on the left-hand side of the main road toward the city of Karak.

2.2. Shale oil collection procedure

Chunks of oil shale were crushed to a smaller size, followed by sieving and particle-size selection for the pyrolysis runs. A mixture of particle sizes ranging from 5 to 8 mm was selected for pyrolysis and shale oil generation. 400 g of oil shale was placed in the retort. The retort was maintained under a nitrogen gas environment at a constant flow rate supplied from a nitrogen gas cylinder. The flow rate of nitrogen gas was kept at a minimum to ensure the continuous transport of the generated hydrocarbon vapors from the pyrolysis zone, thereby minimizing secondary cracking reactions and maximizing the condensation of these vapors as they passed through the glass condenser by reducing their residence time inside the condenser. Oil shale pyrolysis experiments were conducted at a final temperature of 550 °C using a fixed heating rate of 10 °C/min for all runs. The hydrocarbon vapors were passed through a glass condenser cooled by water circulating at a temperature of 5 °C. The condensed shale oil was collected in a graduated cylinder at the bottom of the retort. The produced gases and uncondensed light hydrocarbons were released without further treatment. Several experimental runs were conducted to generate a sufficient amount of shale oil for the whole ionic liquid–shale oil extraction process. A minimum of 200 mL of shale oil was collected for the extraction of sulfur from shale oil using both target ILs.

A known quantity of shale oil and a known quantity of IL were mixed according to the specified IL/SO volume ratio. The mixing process was conducted at the desired experimental temperature for extraction. This part of the experiment was performed for both shale oil samples and both types of ILs investigated. The mixture was heated in a temperature-controlled water bath. The heated mixture was allowed to cool and separate into two phases.

The total amount of sulfur removed was determined using a Euro Vector 3000 CHNS-O elemental analyzer. Individual sulfur components in the shale oil were detected by gas chromatography–mass spectrometry (GC–MS) using an Agilent 7890 and Shimadzu’s GCMS-TQ8030.

2.3. Liquid–liquid extraction of shale oil

Two types of ILs were employed to extract sulfur compounds from shale oil. The ILs were 3-butyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate ([BMIM]BF₄) with the chemical formula C₈H₁₅BF₄N₂, a purity of >98%, a molecular weight of 226.02 g/mol, and a density of 1.20 g/mL, and 1-butyl-3-methyl-1H-imidazol-3-ium hexafluorophosphate ([BMIM]PF₆) with the chemical formula C₈H₁₅F₆N₂P, a purity of >99.98%, a molecular weight of 284.18 g/mol, and a density of 1.38 g/mL. Both ILs were purchased from BLD Pharma Tech GmbH, Germany.

Liquid–liquid extraction was performed using [BMIM]BF₄ and [BMIM]PF₆ as the extracting agents. The extraction process variables were extraction temperature (20, 40, and 60 °C), the IL/SO volume ratio (1.0:1.0, 1.0:3.0, 1.0:5.0, 1.0:8.0, and 1.0:10.0), and IL type ([BMIM]BF₄ or [BMIM]PF₆), with a fixed extraction time of 30 min. A measured volume of shale oil was placed in a glass vial, and the appropriate volume of IL was then injected into the shale oil vial according to the predetermined IL/SO volume ratio. The mixture was thoroughly shaken and placed in a water bath at the desired experimental temperature for 30 min. At the end of the extraction process, the two phases were separated by centrifugation immediately prior to measuring their sulfur contents. The sulfur contents of both the treated shale oil and IL layers were determined using a Euro Vector 3000 CHNS-O elemental analyzer. The sulfur content, expressed as weight percentage, of the original shale oil was also determined for the whole collected sample. Table 1 presents the detailed experimental conditions, namely, temperature, IL/SO volume ratio, and IL type. A total of 52 experimental measurements were conducted. The total sulfur contents of the generated Attarat and El-Lajjun shale oils were determined to be 12.1 and 11.2 wt.%, respectively.

The resulting mixture was separated into a sulfur-depleted shale oil layer and a sulfur-rich ionic liquid layer. The sulfur content of each layer was measured as total sulfur rather than as individual sulfur compounds.

Table 1. Shale oil–ionic liquid extraction conditions: IL/SO volume ratios and extraction temperatures at a fixed extraction time

	[BMIM]BF ₄	[BMIM]PF ₆	IL/SO volume ratio	Temperature, °C	Time, min
Attarat					30
Shale oil layer	1, 1, 1	1, 1, 1	1:1	20, 40, 60	
	1, 1	1, 1	1:3	40, 60	
	1	1	1:5	40	
	1	1	1:8	40	
	1	1	1:10	40	
Ionic liquid layer	1, 1, 1	1, 1, 1	1:1	20, 40, 60	
	1, 1	1, 1	1:3	40, 60	
	1	1	1:5	40	
	1	1	1:8	40	
	1	1	1:10	40	
El-Lajjun					
Shale oil layer	1, 1, 1	1, 1, 1	1:1	20, 40, 60	
	1, 1	1, 1	1:3	40, 60	
	1	1	1:5	40	
Ionic liquid layer	1, 1, 1	1, 1, 1	1:1	20, 40, 60	
	1, 1	1, 1	1:3	40, 60	
	1	1	1:5	40	

3. Results and discussion

The ILs used in this study were organic salts that exist in the liquid phase. They are composed of a common heterocyclic organic cation, [BMIM]⁺, and inorganic anions such as [BF₄][−] and [PF₆][−] in the present investigation. One method for removing sulfur compounds from crude oils or fuels is the use of ILs via extractive desulfurization [28]. Strongly electrostatically charged sulfur-containing molecules are attracted to bipolar ILs. This interaction leads to the separation of selected sulfur-containing compounds from shale oil. The chemical potential difference between the shale oil and IL phases, as reflected in the partition coefficient and Gibbs free energy [29], drives separation in this nonreactive process. Compounds such as thiophene and/or its derivatives, benzothiophenes and/or their derivatives, and other mercaptans

migrate into the IL phase through π – π stacking, hydrogen bonding, and dipole–dipole interactions [30, 31]. The preceding discussion is based on studies of systems other than shale oil, particularly systems with low sulfur content and/or model fuels. Future work will focus on investigating the removal of individual sulfur compounds from shale oil using more sophisticated instruments such as gas chromatography–mass spectrometry with sulfur chemiluminescence detection (GC–MS–SCD), as well as on studying the different fractions obtained from shale oil distillation. A mechanistic investigation of the extraction process requires further development and preplanned experiments.

3.1. Effect of temperature on extraction

3.1.1. Attarat shale oil

The results obtained in the present work are presented in the following subsections. The two shale oils were mixed with ILs at different temperatures, different IL/SO volume ratios, and using different ILs, as indicated in Table 1. The effect of mixing the ILs with Attarat shale oil at different temperatures is depicted in Figure 1. Initially, the original shale oils from both samples were analyzed to determine their sulfur contents on a weight basis. The Attarat and El-Lajjun shale oils were found to contain 12.1 and 11.2 wt.% sulfur, respectively. The subsequent sulfur recovery or removal percentages were calculated based on these values. The results displayed in Figure 1 indicate that the highest sulfur removal efficiency from Attarat shale oil using [BMIM]PF₆ was 62.81% at 40 °C and an IL/SO volume ratio of 1.0:1.0. By comparison, a sulfur removal efficiency of 57.9% was obtained with [BMIM]BF₄ under the same conditions.

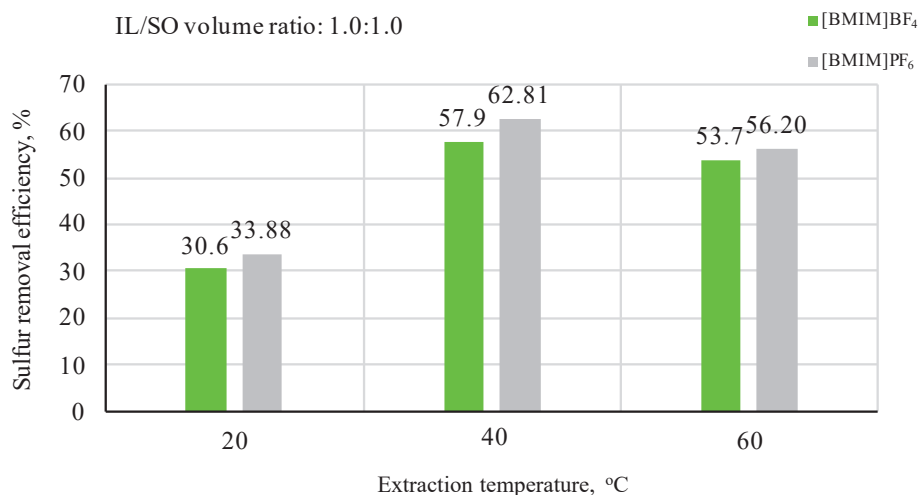


Fig. 1. Attarat sulfur removal efficiency as a function of extraction temperature.

On the other hand, the removal efficiencies at 60 °C and an IL/SO volume ratio of 1.0:1.0 using [BMIM]PF₆ and [BMIM]BF₄ were 56.2% and 53.7%, respectively. It is clear that extraction at 40 °C resulted in a slightly higher removal efficiency. This difference in removal efficiency between the two ILs may be attributed to the nature and physical properties of the inorganic anions of the ILs, i.e., the [PF₆]⁻ group, or to the concentration and type of organosulfur compounds present. Investigators experimentally measured the viscosities of [BMIM]PF₆ and [BMIM]BF₄ at 20, 40, and 60 °C and reported that the viscosity of [BMIM]PF₆ was almost 2.9 times higher than that of [BMIM]BF₄ at 20 °C and 2.4 and 2.2 times higher at 40 and 60 °C, respectively, at a pressure of 0.1 MPa [32]. Although the viscosity of Attarat shale oil was not measured in this work, in general, increasing the temperature can improve and facilitate the extraction process. The removal efficiency almost doubled when the mixing temperature was increased from 20 to 40 °C. Lowering the viscosity enhances the mobility of the inorganic anions of the ILs and facilitates the mobility of the shale oil. In contrast, the removal efficiency decreased by almost 10% when the temperature increased from 40 to 60 °C, despite the associated reduction in viscosity.

3.1.2. El-Lajjun shale oil

The extraction of sulfur compounds from shale oil using ILs at different temperatures is presented in Figure 2. The extraction results for El-Lajjun shale oil were similar to those for Attarat shale oil. As shown in Figure 2, a removal efficiency of 65.2% was achieved with [BMIM]PF₆ at 40 °C and an IL/SO volume ratio of 1.0:1.0. The removal efficiency reached a maximum at 40 °C, increasing from 27.7% at 20 °C to 65.2%, corresponding to a 2.35-fold increase for [BMIM]PF₆ and a 2.46-fold increase for [BMIM]BF₄ when

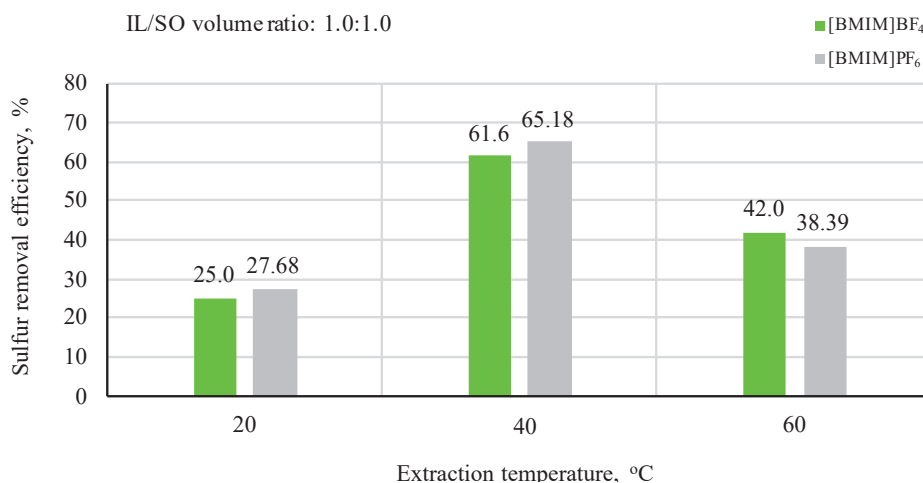


Fig. 2. El-Lajjun sulfur removal efficiency as a function of the ionic liquid–shale oil extraction temperature.

the temperature was increased from 20 to 40 °C. The cation [BMIM]⁺ and anion BF₄⁻ of the IL are smaller, with an anion having higher charge density compared with [BMIM]⁺ and PF₆⁻ IL. Differences in the physical and chemical properties of the ILs, such as viscosity and cation and anion characteristics, may enhance extraction. The difference in the magnitude of the removal efficiency between Attarat and El-Lajjun shale oils for the same IL may be attributed to the nature and concentration of sulfur compounds present in the respective shale oils. Furthermore, the reduction in efficiency when the temperature increased from 40 to 60 °C was 26.8% and 19.6% for [BMIM]PF₆ and [BMIM]BF₄, respectively.

The reduction in efficiency was greater than that observed for Attarat shale oil under the same experimental conditions. For Attarat shale oil, the reduction in removal efficiency was 9% and 7% for [BMIM]PF₆ and [BMIM]BF₄, respectively, when the extraction temperature was increased from 40 to 60 °C. This greater reduction for El-Lajjun shale oil may be attributed to the types and quantities of organosulfur compounds available for extraction by the specific IL and to changes in viscosity with increasing temperature. It is clear from Figures 1 and 2 that the removal efficiency was higher for Attarat shale oil than for El-Lajjun shale oil under the same experimental conditions. The difference in removal efficiency between the two shales oils may be ascribed to differences in composition and the ability of the ILs to selectively extract compounds. Table 2 presents the sulfur compounds detected in the shale oils by GC–MS using reference standards. The same compounds were present in different percentages of the two oils, which may have affected the removal efficiency for each oil.

Inspection of Table 2 shows that the weight percentage of several compounds differed between the two shale oils. For example, dibenzothiophene in Attarat shale oil is estimated at 1.76 wt.% of the total detected organosulfur compounds in the standard components during GC–MS analysis, whereas the corresponding value in El-Lajjun shale oil was 2.9 wt.%, which is almost 1.6 times that in Attarat shale oil. Similarly, comparison of thiophene, 2,3,4-trimethyl, and 2,3-dimethyl-benzothiophene showed that their weight percentages were approximately the same in the two shale oils. On the other hand, amounts of thiophene, 2-decyl and thiophene, 2-(2-methylpropyl) were 20% lower in Attarat and 25% higher in El-Lajjun shale oils. Differences in the weight percentages of these compounds could lead to differences in removal efficiency if an IL has a greater affinity for certain organosulfur compounds.

According to Table 2, GC–MS analysis of the original Attarat shale oil indicated that the thiophene, 2-decyl (C₁₄H₂₄S) concentration, measured as an area percentage, was equivalent to 24.37% of the total sulfur content. After sulfur extraction with [BMIM]PF₆ and [BMIM]BF₄, the measured areas for the same component were 1.56% and 3.7%, respectively, indicating a reduction in concentration. The total sulfur content in the original Attarat and El-Lajjun shale oils was found to be 11.9 and 10.7 wt.%, respectively. For example,

Table 2. Selected sulfur compounds detected in Attarat and El-Lajjun shale oils after extraction with [BMIM]PF₆ and [BMIM]BF₄

Organosulfur compound	Chemical formula	Attarat shale oil	Oil layer with [BMIM]PF ₆		El-Lajjun shale oil	Oil layer with [BMIM]BF ₄	
			[BMIM]PF ₆	[BMIM]BF ₄		[BMIM]PF ₆	[BMIM]BF ₄
Total sulfur, wt. %		11.9	7.0	8.1	10.7	6.3	5.9
Chromatogram area, %							
Thiophene, 2-decyl	C ₁₄ H ₂₄ S	24.37	1.56	3.7	19.63	1.26	0.17
Thiophene, 2,3,4-trimethyl	C ₇ H ₁₀ S	15.13	17.07	18.52	14.02	25.24	16.92
Thiophene, 2-(2-methylpropyl)	C ₈ H ₁₂ S	9.66	17.07	19.75	12.15	14.2	18.62
Thiophene, 2-(1-methylethyl)	C ₇ H ₁₀ S	1.09	1.56	1.23	8.22	3.15	2.54
Dibenzothiophene	C ₁₂ H ₈ S	1.76	2.84	3.09	2.9	2.84	4.06
2,3-dimethyl-benzothiophene	C ₁₀ H ₁₀ S	9.66	9.96	6.17	9.35	6.47	9.31

the Attarat shale oil layer after extraction with [BMIM]PF₆ was found to contain 7.0 wt.% total sulfur, and when the thiophene, 2-decyl component was monitored within the entire spectrum of sulfur components, the GC–MS chromatogram gave an area of 1.56%. When Attarat shale oil was treated with [BMIM]BF₄, the corresponding results were 8.10 wt.% total sulfur and an area of 3.7% for thiophene, 2-decyl in the GC–MS chromatogram. The area shares of the thiophene, 2-decyl component in the 11.9 and 10.7 wt.% values were 24.37% and 19.63%, respectively, of the total sulfur compounds detected in the original shale oil samples using GC–MS analysis.

Simple calculations based on these values show that the amount of the thiophene, 2-decyl component present in the Attarat shale oil was 2.9 g per 100 g of shale oil; after extraction with [BMIM]BF₄, it was 0.44 g per 100 g of the shale oil phase. This result indicates an 84.8% removal efficiency for the target component. Similarly, during the [BMIM]PF₆ extraction process, when the thiophene, 2-decyl component was traced, the measured GC–MS area corresponded to 0.11 g per 100 g of shale oil, indicating a 96.2% removal efficiency. Similar calculations can be performed for the El-Lajjun shale oil sample.

The extraction of 2,3-dimethyl-benzothiophene (C₁₀H₁₀S) is also clear, as indicated in columns 3, 4, and 5 of Table 2. From the tabulated data, the presence of the two afore-mentioned components is more prominent compared to the other compounds indicated in Table 2. This qualitative analysis provides an indication of the extraction preferences for different sulfur compounds. El-Lajjun shale oil exhibited similar trends for the C₁₄H₂₄S and C₁₀H₁₀S components, whereas the extraction of thiophene, 2-(1-methylethyl) (C₇H₁₀S) and 2,3-dimethyl-benzothiophene (C₁₀H₁₀S) was less prominent, and the extraction trends were dependent on the IL type. The El-Lajjun results are displayed in columns 6, 7, and 8 of Table 2.

Simple numerical calculations for the extraction of 2,3-dimethyl-benzothiophene from El-Lajjun shale oil show that 1.0 g was present in the original sample, of which 0.41 g was not extracted, resulting in a 59% removal efficiency with [BMIM]PF₆. With [BMIM]BF₄, the calculated amount not extracted was 0.55 g out of the 1.0 g originally present, corresponding to an extraction efficiency of 45%. This indicates that the composition of the shale oil and the type of IL play a vital role in the extraction process. The ionic liquid–shale oil interaction mechanism, the size of the anionic fraction of the IL, viscosity, and other physical properties might also influence the process. Further investigation on the role of IL interactions with certain organosulfur compounds, including the possibility of synthesizing a model oil to test the extraction preferences of certain ILs for specific compounds. A more thorough investigation and tracing of individual components during the extraction process would provide a better understanding of the mechanism, interactions, and removal efficiency of sulfur components.

3.1.3. Effect of ionic liquid type

The effect of ionic liquid type on the extraction efficiency is depicted in Figure 3. The results shown in Figure 3 indicate that the highest removal efficiency was recorded with [BMIM]PF₆ for El-Lajjun shale oil at 40 °C with an IL/SO volume ratio of 1.0:1.0, with efficiencies exceeding 65% and reaching 62.8% for El-Lajjun and Attarat, respectively. Apparently, the extraction characteristics of [BMIM]PF₆ in terms of anion size, dipole, and other properties may be more favorable for certain sulfur compounds that are present at higher concentrations in Attarat shale oil. This conclusion is supported by the higher removal efficiencies indicated in Figure 3, where the removal efficiencies for [BMIM]PF₆ were 33.88% and 56.2%, the highest values obtained for Attarat shale oil at 20 and 60 °C, respectively.

The extraction mechanism has been described by several authors [17, 22–24]. In one study, the absorption of thiophenes (thiophene and methylthiophene) by ILs, expressed as the molar thiophene/IL ratio, was found by NMR analysis to be 3.5:1 and 2.2:1 for [BMIM]⁺PF₆[−] and [BMIM]⁺PBF₄[−], respectively [17]. Other authors reported an 11.0% sulfur removal efficiency using a model oil at room temperature with [BMIM]BF₄ [24]. These interactions promote high solubility of the sulfur species in the extraction phase, leading to efficient separation from the IL matrix [25]. Furthermore, the structural rigidity and low reactivity of these compounds prevent irreversible interactions with the IL, facilitating its smooth regeneration. Recent studies have found that the extraction efficiencies of the sulfur compounds thiophene and dibenzothiophene appear to correlate with the volume of the anion [26]. The extraction efficiencies of thiophene and dibenzothiophene using

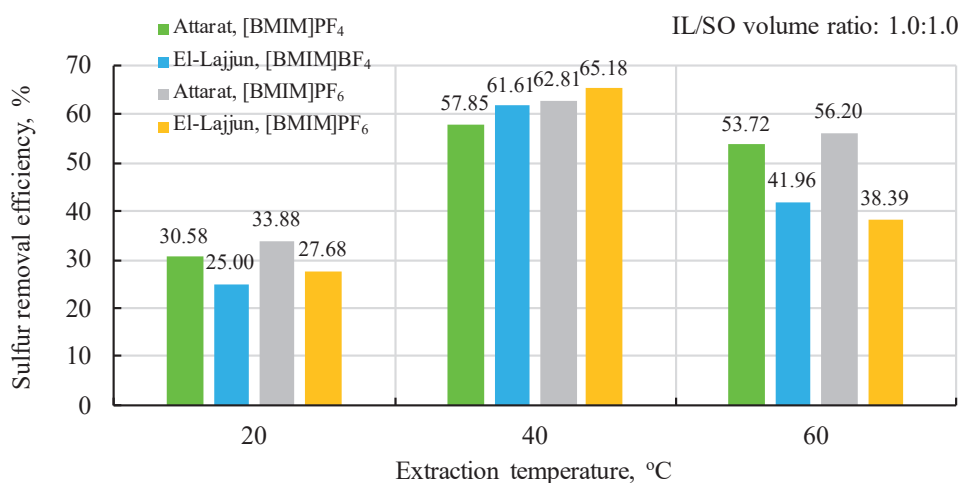


Fig. 3. Sulfur removal percentage as a function of ionic liquid type at different temperatures.

[BMIM]PF₆ were reported to be 31.24% and 25.87%, respectively, whereas the corresponding values were 24.8% and 19.51% using [BMIM]BF₄, respectively [27]. The estimated anionic volumes of [PF₆]⁻ and [BF₄]⁻ were 0.109 and 0.073 nm³, respectively. The common cationic volume of [BMIM]⁺ in both ILs was 0.196 nm³. These volumes show that the anion volume of [PF₆]⁻ is 1.5 times that of [BF₄]⁻, which might contribute to the differences in the extraction mechanism or selectivity for sulfur compounds.

In the present work, thiophene and dibenzothiophene were present, and both [BMIM]PF₆ and [BMIM]BF₄ were used, which may explain the better sulfur removal efficiency as reported. One limitation of the present study is the absence of viscosity measurements for shale oils. However, the viscosity of the shale oils is also expected to improve with increasing temperature, as may be reflected in the removal efficiency results obtained at 20 and 40 °C. These dynamic interactions, together with differences in molecular size, temperature, and viscosity, promote high solubility of the sulfur species in the extraction phase, resulting in efficient separation from the IL matrix. Furthermore, the structural rigidity and low reactivity of these compounds prevent irreversible interactions with the IL, facilitating its smooth regeneration [25].

3.1.4. Effect of the IL/SO volume ratio

The effect of increasing the IL/SO volume ratio from 1.0:1.0 to 1.0:10.0 at 40 °C on the sulfur removed, expressed as weight percentage, from Attarat shale oil is depicted in Figure 4. It is clear from the values depicted in the graph and the visible trend of the columns that increasing the IL/SO volume ratio decreases the weight percentage of sulfur removed. It is also clear from the figure that the values obtained at the 1.0:5.0 IL/SO volume ratio, 7.1

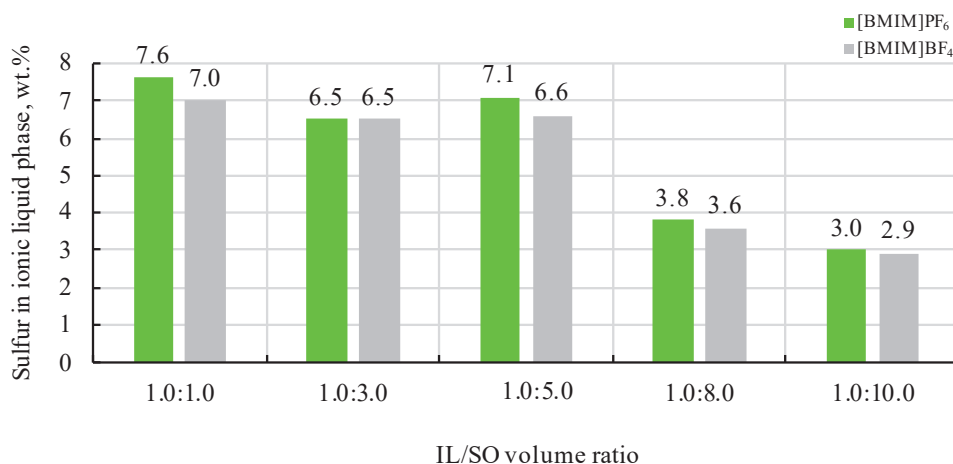


Fig. 4. Effect of the IL/SO volume ratio on the weight percentage of sulfur removed from Attarat shale oil at 40 °C.

and 6.6 wt.%, are close to the values of 7.6 and 7.0 wt.% obtained at the 1.0:1.0 IL/SO volume ratio, amounting to more than 93% of the corresponding values. The 1.0:5.0 ratio is more economical than the 1.0:1.0 ratio, since the quantity of shale oil treated is five times greater than that at the 1.0:1.0 IL/SO volume ratio. The data points presented as columns in Figure 4 are the weight percentages measured in the ionic liquid layer. The removal efficiency is calculated by dividing these values by 12.1 wt.%, as indicated at the top left of the figure.

4. Conclusions

Two ionic liquids, [BMIM]PF₆ and [BMIM]BF₄, were used to extract sulfur compounds from shale oils obtained by pyrolysis of oil shale from Attarat and El-Lajjun regions. The two ILs were able to extract sulfur-bearing hydrocarbons from the shale oils with varying degrees of removal efficiency. The sulfur contents in the original shale oils, the extracted shale oil phase, and the ionic liquid-rich phase were measured as total sulfur. The removal efficiencies were found to be highest, exceeding 55% at an extraction temperature of 40 °C, compared with those obtained at 20 and 60 °C. The optimum IL/SO volume ratio was found to be 1.0:5.0, at which the efficiency was only slightly lower than that obtained at an IL/SO volume ratio of 1.0:1.0. [BMIM]PF₆ resulted in higher removal efficiencies at 40 °C than [BMIM]BF₄. The maximum removal efficiencies reported for [BMIM]PF₆ and [BMIM]BF₄ were 65.2% and 61.6%, respectively, for El-Lajjun shale oil, and 62.8% and 57.9%, respectively, for Attarat shale oil at 40 °C.

Further studies are required to investigate the regeneration and recyclability of the ionic liquids to improve the economic feasibility of any future industrial application. In addition, the selectivity of each ionic liquid for different sulfur compounds needs to be investigated.

Data availability statement

All data used in this article are publicly available. No new data were created or analyzed in this study.

Acknowledgments

The publication costs of this article were partially covered by the Estonian Academy of Sciences.

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Oil shale semi-coke-activated persulphate treatment of aniline wastewater: feasibility and reaction mechanism

Wenjing Wang^(a), Guozheng Zhao^(a), Yanhui Song^(b), Changbo Li^{(a)*}, Liguang Xiao^(c)

^(a) School of Environmental and Safety Engineering, Liaoning Petrochemical University, Fushun 113001, China

^(b) China National Petroleum Corporation Fushun Petrochemical Branch, Fushun 113008, China

^(c) Fushun Mining Group Co., Ltd. Engineering Technology Research Centre, Fushun 113005, China

Received 2 August 2025, accepted 21 October 2026, available online 23 October 2026

Abstract. *This study employed oil shale semi-coke (OSSC), a solid waste from oil shale pyrolysis, as a persulphate (PS) activator for the treatment of aniline wastewater. The catalyst was characterized by scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) analysis, and X-ray photoelectron spectroscopy (XPS), etc., which revealed its porous structure along with the presence of low-valent iron and organic components. The research evaluated its catalytic performance, optimized the degradation process, and elucidated the reaction mechanisms. Under the optimized conditions of an OSSC dosage of 5 g/L, a PS concentration of 7.5 mM, an initial pH of 3, and a temperature of 80 °C, complete removal of aniline was achieved within 60 minutes. Mechanistic analysis indicated that the system operates via synergistic radical and non-radical pathways. The low-valent iron in OSSC activates PS to generate reactive oxygen species such as $\text{SO}_4^{\bullet-}$, $\bullet\text{OH}$, $\text{O}_2^{\bullet-}$, thereby initiating the oxidative polymerisation of aniline. The resulting polyaniline-like polymers are effectively immobilized onto the OSSC matrix, forming a composite material. This work provides new insights into the reaction mechanisms of heterogeneous PS activation systems and proposes a promising waste-treats-waste strategy for the resource utilisation of OSSC and the degradation of aniline.*

Keywords: oil shale semi-coke, waste treatment with waste, persulphate, aniline, oxidative polymerisation.

* Corresponding author, lnpnlcb@126.com

1. Introduction

China possesses abundant oil shale resources, with deposits primarily distributed in the Maoming, Huadian, Fushun, and Longkou regions, where they can be converted into shale oil and fuel gas through pyrolysis, making it an important alternative petroleum resource [1]. However, oil shale has a high degree of mineralisation and a low oil content, and the pyrolysis process produces large amounts of oil shale semi-coke (OSSC). Research [2] indicates that every tonne of shale oil produced is accompanied by 10–30 tonnes of OSSC. Currently, there are no large-scale resource utilisation methods, leading to the continuous accumulation of OSSC, causing severe pollution and the waste of resources and land. Therefore, converting low-value solid waste into high-value functional materials is crucial for achieving sustainable industrial development. OSSC possesses a developed pore structure, high structural stability, low particle density and high bulk density, low moisture content (0.27–8.53%), low loss on ignition, and excellent grinding and processing performance, demonstrating potential for the preparation of functional materials [3]. Its resource utilisation primarily includes the following applications: secondary combustion [4]; co-combustion with other materials [5–7]; construction materials [8, 9]; agricultural water-retaining agents [10–12]; composting materials [13]; pigments [14]; and chemical raw materials [15, 16]. In water treatment, it is primarily used as an adsorbent [17, 18]. Research indicates that aromatic hydrocarbon biomarkers in oil shale are significantly correlated with maturity [19]. As a pyrolysis product of oil shale, the residual organic matter in OSSC, which has an organic carbon content of approximately 3–6% on a dry basis [20–22], may retain aromatic structures formed during high-temperature evolution and thereby possess potentially catalytic active sites [23]. This provides the theoretical basis for its direct application as a persulphate (PS) catalyst in this study.

Aniline, as an important chemical raw material, is widely used in industries such as dyes, pharmaceuticals, and pesticides. However, it poses significant risks to human health and the environment. On 27 October 2017, the International Agency for Research on Cancer of the World Health Organization listed aniline in the preliminary list of Group 3 carcinogens [24–26]. Oil shale retorting wastewater contains large amounts of aniline and other difficult-to-degrade toxic organic compounds [27]. While the treatment of aniline-containing wastewater typically relies on methods such as adsorption, biodegradation, and chemical oxidation, advanced oxidation processes have gained significant research interest due to their strong oxidising capacity, rapid reaction rates, and ability to improve wastewater biodegradability [28].

The advanced oxidation process based on persulphates is favoured by many scholars because it can generate sulphate radicals ($\text{SO}_4^{\bullet-}$) with an oxidation-reduction potential of 2.5–3.1 V, second only to hydroxyl radicals ($\bullet\text{OH}$), as well as a longer half-life (30–40 ms), enabling more effective degradation

of stubborn pollutants [29]. Moreover, persulphates are easy to transport and store, with simpler operation and control. PS can be activated by various means (e.g. heat, UV, ultrasound, alkali, metals, and carbon materials), each with distinct mechanisms and suitability, allowing for adaptable wastewater treatment design [30]. Despite the variety of activation methods, developing solid waste-derived catalysts that are highly efficient, stable, and require no complex modification is crucial for reducing process costs. Recent studies [31] have shown that pollutants in heterogeneous catalytic oxidation systems are primarily removed through oxidative coupling and polymerisation reactions, rather than through a single mineralisation pathway. The direct oxidation transfer technology based on the oxidative polymerisation pathway can significantly reduce oxidant consumption, energy requirements, and CO₂ emissions, providing a new direction for efficient water treatment.

This study employs raw OSSC, a solid by-product from the pyrolysis (500–600 °C) of oil shale by the Fushun Mining Group, without additional modification, to explore its potential as a PS activator for aniline degradation. The work focuses on: (i) evaluating the catalytic activity of pristine OSSC; (ii) optimising the aniline degradation process; and (iii) elucidating the underlying reaction mechanisms. It aims to directly probe the inherent catalytic properties of OSSC, thereby providing support for the valorisation of solid waste and the development of cost-effective water treatment technologies.

2. Materials and methods

2.1. Reagent

The chemical reagents used in this study were as follows. The following reagents were purchased from Shanghai McLean Biochemical Technology Co., Ltd.: N-(1-naphthyl)ethylenediamine hydrochloride, *p*-benzoquinone, furfuryl alcohol, potassium hydrogen sulphate, and ammonium sulphate. The following reagents were purchased from Tianjin Damiao Chemical Reagent Factory: aniline, sodium nitrate, and sodium nitrite. Methanol and tert-butanol were purchased from Tianjin Hengxing Co., Ltd. The following reagents were purchased from Sinopharm Chemical Reagent Co., Ltd.: sodium chloride, sodium bicarbonate, sodium sulphate, sodium hydroxide, and potassium persulphate. All reagents were of analytical grade and used without further purification.

2.2. Catalyst preparation

OSSC was sourced from Fushun Mining Group Co., Ltd. It is a solid waste by-product generated during the dry distillation of oil shale at approximately 500–600 °C for oil refining. The OSSC was first crushed using a crusher, then screened using sieves of different mesh sizes. The 140–160 mesh OSSC

was alternately washed with dilute hydrochloric acid and deionised water to remove residual pyrolysis products and impurities from the surface. Finally, the OSSC was dried in an oven at 70 °C for 3 h. Subsequently, it was ground and passed through a 140–160-mesh sieve again to ensure a consistent particle size, and then stored for later use.

2.3. Experimental methods

All batch experiments were conducted in triplicate. The reported data are mean values, with standard deviations presented as error bars in the figures. Unless otherwise specified, the following general experimental procedure was used. Predetermined amounts of OSSC and potassium persulphate were added to a 200-mL conical flask. The reaction was initiated by injecting 100 mL of an aniline solution with an initial concentration of 100 mg/L. The flask was then placed in a constant-temperature water bath with magnetic stirring at a fixed speed. After a predetermined reaction time, generally 60 min unless otherwise specified, a 4–5-mL aliquot was withdrawn using a disposable syringe, immediately filtered through a 0.45- μ m aqueous membrane filter, and subsequently analysed for aniline concentration.

System performance comparison: To evaluate the catalytic role of OSSC, three systems were compared at 30 °C: (1) OSSC alone (5 g/L); (2) PS alone (10 mM); and (3) a combined system of OSSC (5 g/L) and PS (10 mM). Samples were collected and analysed at 5, 10, 20, 40, 60, 90, and 120 min.

Single-factor experiments: The influence of individual operational parameters, including OSSC dosage, PS dosage, temperature, pH, and reaction time, was investigated using the one-variable-at-a-time method. Samples for the reaction time study were collected at various intervals, while all other factor experiments were sampled at 60 min. The pH was adjusted using 0.1 mol/L solutions of HCl or NaOH.

Orthogonal optimisation experiment: An orthogonal array design, designated $L_9(3^4)$ with four factors and three levels, as detailed in Table 1, was employed to optimise the process and analyse the primary, secondary, and interactive effects of the factors. Each experimental run followed the general procedure.

Coexisting ion effects experiment: To examine the influence of common anions, 0.1 mol/L solutions of NaCl, NaHCO_3 , NaNO_3 , or Na_2SO_4 were separately added to the OSSC/PS system to introduce Cl^- , HCO_3^- , NO_3^- , or SO_4^{2-} ions.

Active species quenching experiments: To identify the dominant active species, specific scavengers at a concentration of 0.1 mol/L – methanol, tert-butanol, *p*-benzoquinone, or furfuryl alcohol – were separately introduced into the system under optimal conditions. The quenching effects were evaluated by comparing the resulting aniline removal efficiency.

Table 1. Orthogonal experimental factors and levels

Code	Factor	Level		
		1	2	3
A	OSSC dosage, g/L	1	3	5
B	PS dosage, mM	2.5	5	7.5
C	Temperature, °C	30	50	80
D	pH	3	7	11

2.4. Analytical methods

The concentration of aniline in the post-reaction solution was quantified using the N-(1-naphthyl)ethylenediamine azo spectrophotometric method (GB 11889-89). To investigate the reaction mechanism, a systematic comparative characterisation was conducted between the pristine OSSC before the reaction, subsequently denoted as ‘before reaction’ in the text and figures, and the solid OSSC products obtained after the reaction under optimal conditions of 80 °C, PS = 7.5 mM, OSSC = 5 g/L, and pH = 3, which are correspondingly denoted as ‘after reaction’. These samples were characterised using the following techniques. The specific surface area and pore structure were determined by Brunauer–Emmett–Teller analysis (BET, JWBK200C). Elemental composition was analysed using an elemental analyser (EA, Thermo Fisher). The graphitisation degree was characterised by Raman spectroscopy (DXR spectrometer, Thermo Fisher). Morphology and micro-area composition were examined using scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (SEM-EDS, JSM-6360LA, JEOL). Surface functional groups were analysed by Fourier transform infrared spectroscopy (FTIR, resolution of 1.0–2.0 cm⁻¹). Crystal structure was determined by X-ray diffraction (XRD, Cu K α radiation). Bulk chemical composition was measured using X-ray fluorescence spectroscopy (XRF, S8 Tiger, Bruker). Surface elemental chemical states were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, Thermo Fisher; C 1s peak at 284.8 eV used as the reference). Thermal behaviour was analysed by thermogravimetric-differential thermal analysis (TG-DTA, TA Instruments Q600) with samples (~6.75 mg) heated from room temperature to 1000 °C in air at a heating rate of 10 °C/min. Organic compounds in the post-reaction water were identified using gas chromatography-mass spectrometry (GC-MS, Agilent 6530, injection volume of 1 μ L, detector temperature of 325 °C).

3. Results and discussion

3.1. Structure and composition of OSSC

Figure 1(a)–(b) depicts SEM images at different magnifications, clearly showing that the surface of OSSC is relatively rough, characterised by an irregular layered structure and a porous configuration. This corresponds to the transmission electron microscopy (TEM) images in Figure 1(c)–(d). Additionally, Figure 1(d) shows the distinct pore structure of the OSSC. Based on the scale bar, the pores in the image are approximately 10–20 nm in size, indicating that the OSSC belongs to the category of mesoporous materials.

OSSC belongs to the coal-bearing kaolinite series and is composed of organic matter and various inorganic minerals, such as kaolinite, illite, montmorillonite, quartz, feldspar, and magnetite [4, 22]. It possesses a naturally unique organic-inorganic composite structure [25, 26]. The elemental composition of OSSC was determined using EA. As shown in Figure 2(a), its primary elemental contents are C (5.50 wt%), H (0.89 wt%), N (0.49 wt%), O (6.04 wt%), and S (1.03 wt%). XRF also indicated that the inorganic components of OSSC mainly include SiO_2 , Al_2O_3 , and Fe_2O_3 , while other components, such as K_2O and MnO , are present in relatively small amounts, accounting for only 7.40% (see Fig. 2(b)).

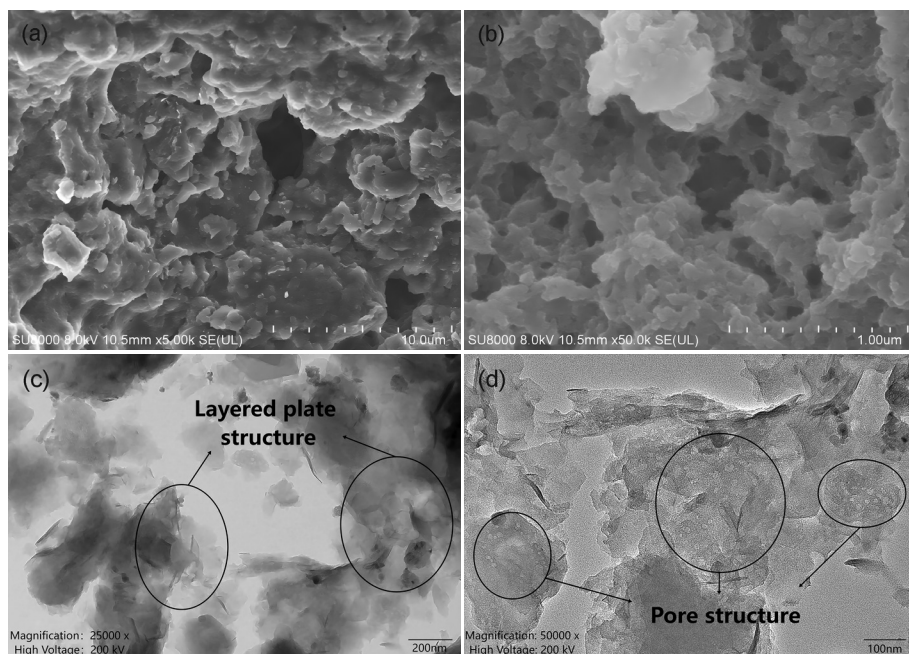


Fig. 1. Scanning electron microscopy images (a, b) and transmission electron microscopy images (c, d) of oil shale semi-coke.

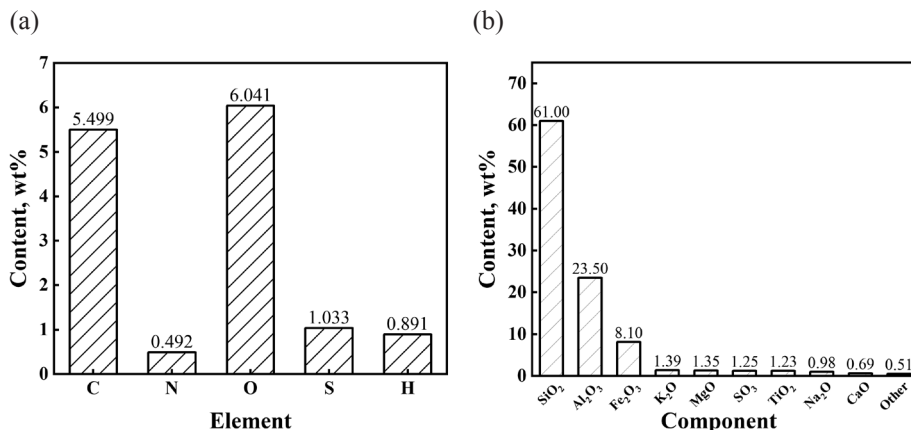


Fig. 2. Composition of oil shale semi-coke: (a) elemental analysis; (b) chemical composition.

3.2. Feasibility of OSSC-activated PS treatment of aniline wastewater

To evaluate the catalytic performance of OSSC, three sets of experiments were conducted following the procedure described in Section 2.3: OSSC alone, PS alone, and PS combined with OSSC (OSSC + PS). As shown in Figure 3, the OSSC-alone system exhibited negligible aniline removal, with only 5.1% removal after 120 min, which may be attributed to the adsorption capacity of OSSC for aniline. In the PS-alone system, the aniline removal reached 37.1% after 120 min, which may be attributed to the oxidative effect of PS on aniline, but its effectiveness requires further enhancement. In the OSSC + PS system, the removal efficiency significantly improved, reaching 50.5% after 5 min and as high as 98.9% after 120 min. The above results indicate that OSSC effectively activates PS for the oxidative degradation of aniline in water.

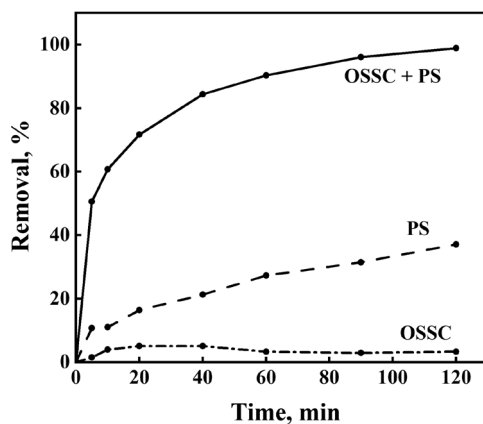


Fig. 3. Removal of aniline by different systems.

3.3. Impact of different factors on the OSSC/PS system

The effects of various factors on the OSSC/PS reaction system were investigated, with the results shown in Figure 4(a)–(e). Figure 4(a) illustrates the impact of different OSSC dosages on aniline removal. As the dosage of OSSC increases, the removal of aniline also increases, as the number of active sites rises with increasing OSSC dosage, resulting in an overall upward trend. However, the difference in removal between 5 g/L (90.3%) and 6 g/L (91.4%) is only 1.1%, which may be due to steric hindrance effects caused by excessively high OSSC dosages, resulting in the number of effective reaction activation sites not increasing proportionally with OSSC dosages [32]. Figure 4(b) shows the effect of different PS dosages on aniline removal. Similarly, the removal of aniline increases with increasing PS dosage and eventually stabilises. When the PS dosage is 15 mM, the removal reaches 82.8%. The initial increase may be attributed to the fact that a higher PS dosage can generate more oxidative free radicals under OSSC catalysis, thereby degrading aniline more rapidly and effectively. However, the number of active sites on OSSC is limited, so the removal efficiency eventually plateaus.

Figure 4(c) shows that the removal of aniline increases with time. At 120 min, the removal reaches 85.3%. Figure 4(d) illustrates the effect of pH on aniline removal. It can be observed that under neutral conditions, the removal efficiency is optimal at 76.1%. Under neutral conditions, the OSSC surface carries a negative charge [33], enabling it to adsorb positively charged aniline molecules. Meanwhile, PS can decompose relatively stably to produce $\text{SO}_4^{\bullet-}$, effectively removing aniline. An acidic environment accelerates the decomposition of PS, producing more $\text{SO}_4^{\bullet-}$ [34]. However, excessively high acidity may damage or alter the active sites on the OSSC surface, thereby weakening its catalytic effect on PS decomposition. Under alkaline conditions, $\bullet\text{OH}$ becomes the dominant species, but it may be partially quenched by CO_3^{2-} present in OSSC. Therefore, when the pH reaches 9, the aniline removal becomes unstable. As the pH continues to increase, peroxydisulphate undergoes spontaneous alkaline hydrolysis ($\text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \text{O}_2$), which is detrimental to aniline removal [29, 30]. Figure 4(e) shows the trend of temperature effects on aniline removal. The removal efficiency shows a slight increase in the 30–50 °C range (78.1–82.7%) and a significant increase in the 60–80 °C range (86.4–98.9%). This may be due to higher temperatures making the O–O bonds in PS more prone to breaking, thereby generating more $\text{SO}_4^{\bullet-}$ to participate in the reaction [35], while also accelerating the reaction rate and promoting the reaction.

3.4. Coexisting ion effects experiment

For coexisting ions, the effects of common ions in industrial wastewater, such as Cl^- , HCO_3^- , NO_3^- , and SO_4^{2-} , on the system were examined, as shown in Figure 4(f). The impact of coexisting ions on aniline removal, from smallest

to largest, is as follows: Cl^- (reduced by 3.6%) < SO_4^{2-} (reduced by 10.4%) < NO_3^- (reduced by 13.7%) < HCO_3^- (reduced by 34.9%). Among these, Cl^- has the least impact on the system, possibly due to its reaction with $\text{SO}_4^{\bullet-}$ to form active chlorine species (e.g. $\text{Cl}^\bullet$), which can partially oxidise the electron-

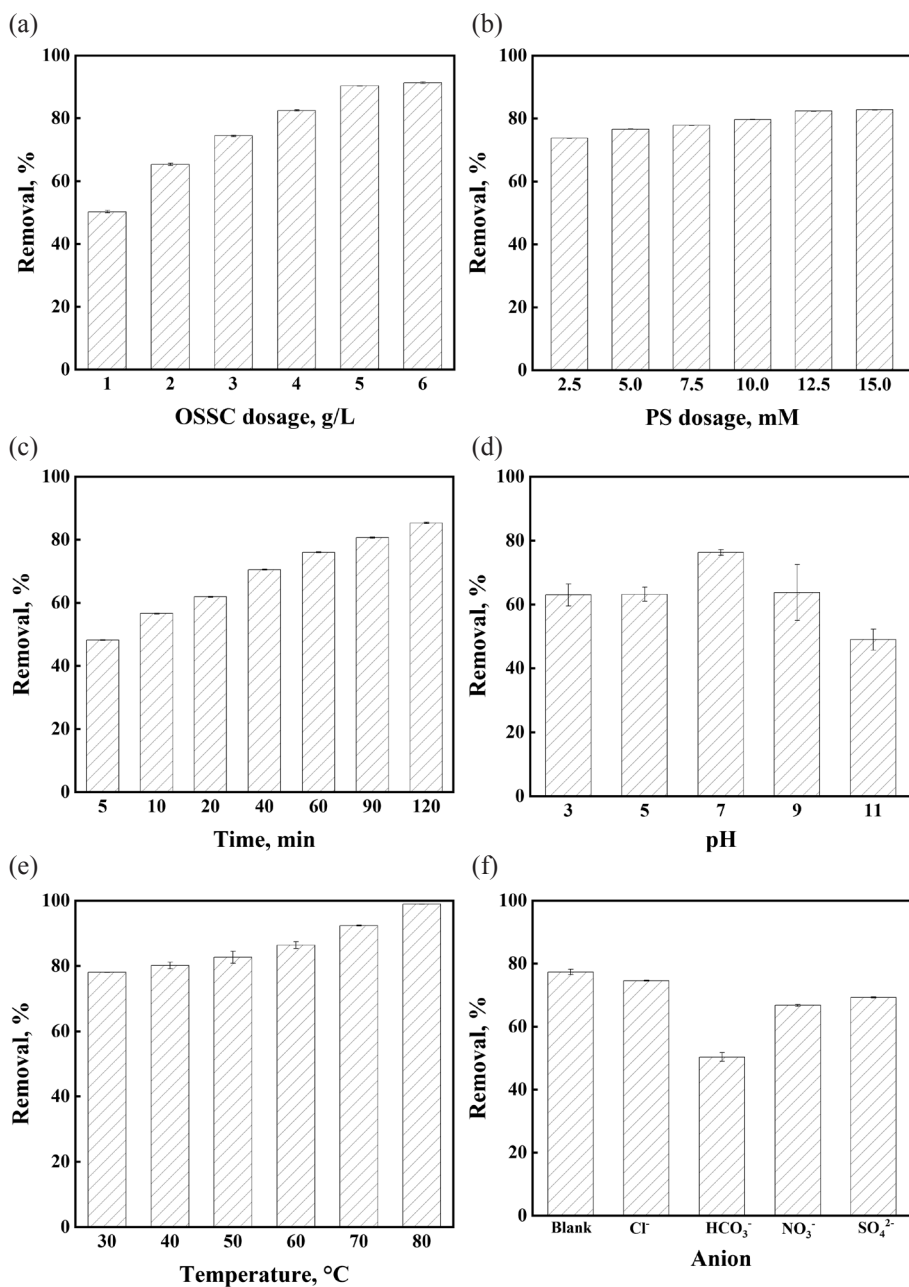


Fig. 4. Effect of different factors on the removal of aniline.

rich aromatic ring of aniline, whereas its small ionic radius causes limited interference with surface adsorption; SO_4^{2-} competes for negatively charged sites on the OSSC surface, leading to a decrease in degradation efficiency. The inhibition caused by NO_3^- may be due to competitive adsorption, and the intermediate products generated by the oxidation of OSSC by NO_3^- may also inhibit the removal of aniline. HCO_3^- exhibits the strongest inhibitory effect, with a removal efficiency of only 50.4%. This may be due to HCO_3^- quenching PS to form low-activity CO_3^{2-} , and the buffering pH of HCO_3^- (approximately 8.3) reduces the protonation of aniline ($\text{pK}_a = 4.6$), weakening electrostatic adsorption and ultimately resulting in the lowest removal efficiency [36, 37].

3.5. Orthogonal optimisation experiment

To better determine the effects of various factors on the reaction system, a four-factor, three-level orthogonal experiment was designed, as shown in Table 2. Based on the principle that the larger the range (R), the more significant the effect of the factor on aniline removal, temperature is the decisive factor in this system (the k value increases by nearly 40% from 30 to 80 °C). PS dosage is the second most important factor, with higher PS concentrations (7.5 mM) significantly promoting the reaction. The pH value has the least impact, possibly due to the reaction system being insensitive to pH. The highest k value levels for each factor were selected: temperature (C), Level 3 (80 °C, $k_3 = 95.66$); PS dosage (B), Level 3 (7.5 mM, $k_3 = 91.51$); OSSC dosage (A), Level 3 (5 g/L, $k_3 = 81.1$); and pH (D), Level 1 (pH = 3, $k_1 = 79.37$). Therefore, the optimal combination was determined to be $\text{C}_3\text{B}_3\text{A}_3\text{D}_1$ (temperature = 80 °C, PS = 7.5 mM, OSSC = 5 g/L, pH = 3). Experimental verification showed that under these conditions, 100% aniline removal was achieved after a 60-min reaction, and the post-reaction solution was nearly colourless, demonstrating excellent decolourisation performance.

Table 2. Orthogonal experimental design matrix and results

No.	OSSC (A), g	PS (B), mM	Temperature, °C	pH (D)	Removal, %
1	0.1	2.5	30	3	38.7
2	0.1	5	50	7	56.2
3	0.1	7.5	80	11	97.4
4	0.3	2.5	50	11	49.7
5	0.3	5	80	3	99.7
6	0.3	7.5	30	7	77.5
7	0.5	2.5	80	7	89.8
8	0.5	5	30	11	53.8
9	0.5	7.5	50	3	99.7

Continued on the next page

Table 2. *Continued*

No.	OSSC (A), g	PS (B), mM	Temperature, °C	pH (D)	Removal, %
k ₁	64.1	59.4	56.7	79.4	
k ₂	75.6	69.9	68.5	74.5	
k ₃	81.1	91.5	95.6	67.0	
R	17.0	32.1	39.0	12.4	

Note: k_x denotes the average removal at each factor level; R denotes the range, indicating the extent of the factor's influence.

To quantitatively evaluate the influence of the operational parameters, a first-order linear regression model was established based on the L₉(3⁴) orthogonal experimental data. The factor levels were coded as -1, 0, and 1 (e.g., for temperature, 30, 50, and 80 °C correspond to -1, 0, and 1, respectively) to facilitate comparison on a unified scale. The regression results are summarised in Table 3, yielding the following model equation:

$$\text{Removal (\%)} = 73.61 + 8.50A + 16.07B + 19.48C - 6.20D \quad (R^2 = 0.957, p < 0.01) \quad (1)$$

This model demonstrates an excellent fit, with a high coefficient of determination ($R^2 = 0.957$) and is statistically significant ($p = 0.005$). The magnitude and sign of the regression coefficients quantitatively reflect the effect of each variable. Temperature (C) is identified as the most influential parameter (coefficient = 19.48), followed by PS concentration ($B = 16.07$) and OSSC dosage ($A = 8.50$). In contrast, pH ($D = -6.20$) exhibits an inhibitory effect under alkaline conditions. This hierarchy of influence ($C > B > A > D$) aligns precisely with the conclusions from the prior range analysis. While the model effectively captures the main effects, it should be noted that potential interaction terms were not included due to the constraints of the orthogonal design; thus, its primary utility lies in trend identification and factor screening.

Table 3. Results of the regression analysis for the orthogonal experiment

Term	Coefficient	Std. error	t-stat	p-value	Significance
Intercept	73.61	2.36	31.23	<0.001	***
A (OSSC dosage)	8.50	2.89	2.94	0.042	*
B (PS dosage)	16.07	2.89	5.57	0.005	**
C (Temperature)	19.48	2.89	6.75	0.003	**
D (pH)	-6.20	2.89	-2.15	0.098	ns

Notes: Std. error – standard error of the coefficient; t-stat – t-statistic for testing the null hypothesis that the coefficient equals zero. Significance levels: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$, and ns – not significant ($p \geq 0.05$). Model fit: $R^2 = 0.957$, adjusted $R^2 = 0.915$, f-statistic = 22.46, model p-value = 0.005.

It is noteworthy that the selection of the optimum temperature (80 °C) suggests a potentially significant contribution from thermal activation within the system. Consequently, a critical question arises: under these optimal conditions, is the activation of PS primarily driven by thermal activation, or does the catalytic action of OSSC play a decisive role? To elucidate this matter, we designed the following comparative experiments.

3.6. Distinguishing OSSC catalysis from thermal activation contributions

To distinguish between the contributions of thermal activation and OSSC-catalysed activation under the optimal conditions, a set of control experiments was conducted. The performance of the full OSSC/PS system (OSSC = 5 g/L, PS = 7.5 mM) was compared with that of PS alone (thermal-activation control) and OSSC alone (adsorption control) at 80 °C and pH 3.

The results are shown in Figure 5. The PS-alone system achieved a final aniline removal of 75.6% in 120 min, representing the baseline efficiency attributable solely to thermal activation. In stark contrast, the OSSC/PS system exhibited drastically enhanced kinetics and efficiency, reaching 66.6% removal within just 5 min and essentially reaching reaction equilibrium with 99.7% removal within 20 min. The OSSC-alone system showed negligible removal (<15%), effectively ruling out adsorption as a primary mechanism.

This direct comparison confirms that the superior performance under optimal conditions arises from synergistic activation: while thermal activation provides a foundation, OSSC acts as an indispensable catalyst, introducing a more efficient pathway that drastically accelerates PS activation and maximises pollutant degradation.

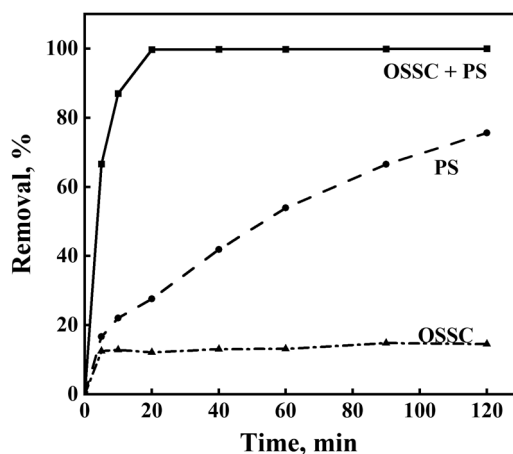


Fig. 5. Time-dependent aniline removal by different systems under optimal conditions.

4. Material characterisation and reaction mechanism

4.1. Evolution of physical properties and pore structure

Table 4 and Figure 6(a) show the N_2 adsorption–desorption isotherms and changes in pore structure parameters before and after the OSSC reaction. The initial adsorption isotherm of OSSC exhibits an inverted S-shaped profile, with adsorption capacity increasing continuously in the low relative pressure range ($P/P_0 < 0.1$), accompanied by H3-type hysteresis loops. This behaviour aligns with the IUPAC (International Union of Pure and Applied Chemistry) Type IV characteristics, indicating that its structure primarily comprises mesopores formed by the aggregation of fissure-like or layered particles [22], consistent with the SEM images (Fig. 1). After the reaction, the adsorption capacity decreases significantly (especially noticeable in the medium-to-high pressure range, where $P/P_0 > 0.4$), and the hysteresis loop transitions from the H3 type to a form closer to the H4 type, with reduced contributions from mesoporous and macroporous adsorption. Table 4 shows that the specific surface area and pore volume decrease significantly after the reaction, while the average pore diameter increases; moreover, the S_{ext} and S_{BET} values were equal (both $16.17 \text{ m}^2/\text{g}$). Combined with Figure 7, this suggests that the micropores and mesopores may have compromised due to filling or collapse, with the remaining pore channels primarily consisting of larger pores. The reduction in pore volume, rather than the expected increase in new pores due to oxidative etching, indicates that the system undergoes more than simple oxidative reactions. The strong oxidising properties of PS under acidic and thermal conditions may have triggered reactions such as aniline oxidation polymerisation, with the reaction products entering and occupying the pore space, leading to the blockage of micropores and some mesopores.

Figure 6(b) shows the TG and DTG analysis results before and after the OSSC reaction. The residual mass percentage of OSSC before and after the reaction is very high, mainly due to the presence of residual inorganic minerals. The DTG curves reveal that the mass-loss step around 100°C ,

Table 4. Comparison of pore structure parameters of oil shale semi-coke before and after the reaction

Parameter Sample	S_{BET} , m^2/g	S_{ext} , m^2/g	Pore volume, cm^3/g	Mean pore size, nm
Before reaction	59.41	39.33	0.12	11.32
After reaction	16.17	16.17	0.07	17.88

Note: S_{BET} – specific surface area calculated by the Brunauer–Emmett–Teller method; S_{ext} – external surface area obtained from the t-plot method.

corresponding to the release of structural water from the pre-dried OSSC, disappears after the reaction. This change suggests that the catalytic process altered the surface or bulk properties of OSSC, potentially due to coverage by oxidation products or a change in surface chemistry, which affected the material's interaction with or retention of structural water. Additionally, after the reaction, OSSC begins to lose mass at a lower temperature (approximately 290 °C), with the TG and DTG curves showing a clear separation. However, at approximately 500 °C, the DTG curve overlaps with that of the original sample, indicating that the carbon skeleton of OSSC is retained, but that new organic components with lower thermal stability have been introduced. This characteristic temperature range (250–300 °C) is highly consistent with the pyrolysis behaviour of polyaniline [38–40], revealing that aniline undergoes oxidative polymerisation during the reaction, forming easily decomposable nitrogen-containing polymers on the OSSC surface, rather than interference from small-molecule aniline (boiling point 184 °C) or residual oxidants.

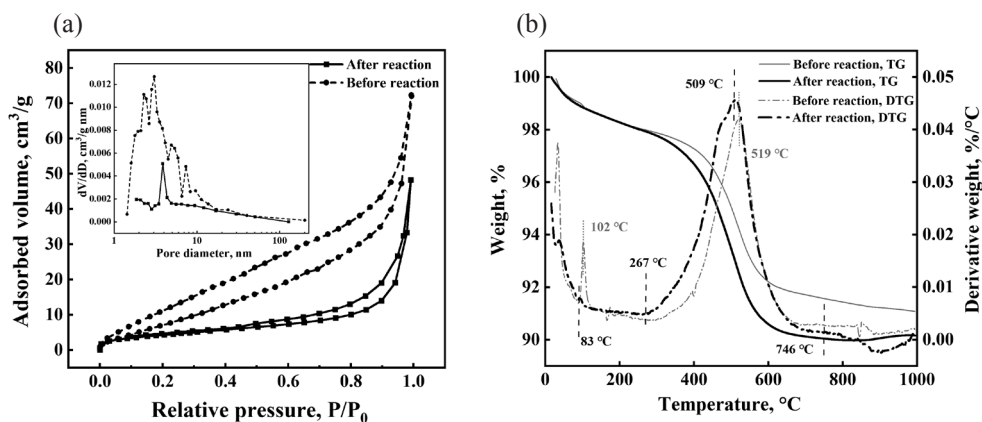


Fig. 6. (a) N_2 adsorption-desorption isotherms; (b) thermogravimetric-derivative thermogravimetric images of oil shale semi-coke before and after the reaction.

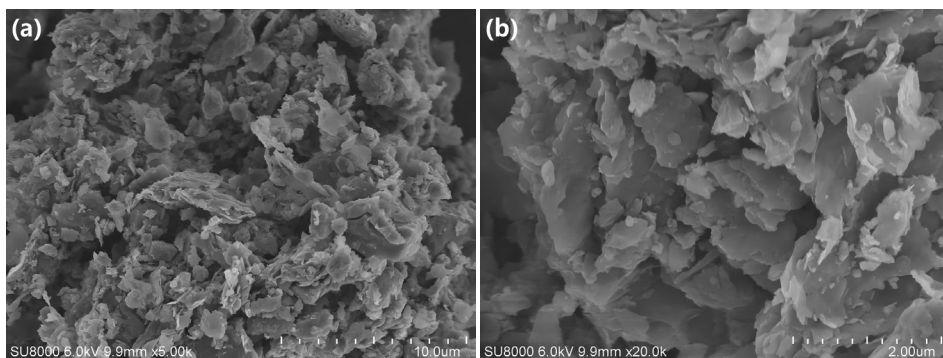


Fig. 7. Scanning electron microscopy images of OSSC after the reaction: (a) low-magnification image (×5K); (b) high-magnification image (×20K).

4.2. Transformation of organic components: evidence of oxidative polymerisation

To elucidate the transformation of organic components during the catalytic process, the structural and compositional changes of OSSC before and after the reaction were analysed using Raman spectroscopy and elemental analysis. The results collectively indicate that aniline underwent oxidative polymerisation and was incorporated into the OSSC matrix.

Figure 8 shows the Raman spectra of OSSC before and after the reaction. The I_D/I_G intensity ratio is a key parameter used to characterise the degree of disorder in carbon materials. The D peak (approximately 1350 cm^{-1}) primarily originates from defects, edges, or disordered structures in the carbon lattice, while the G peak (approximately 1580 cm^{-1}) arises from the in-plane vibrations of sp^2 -hybridised carbon atoms in an ideal graphite lattice, representing ordered structures [41]. After the reaction, the I_D/I_G value decreased from 0.93 to 0.88, indicating an increase in the relative proportion of ordered graphitic structures and a decrease in disordered components. This suggests an overall improvement in the graphitisation degree of the material. The observed ordering aligns with the expected outcome of an oxidative polymerisation pathway, in which small molecules or fragments form larger conjugated systems through dehydrogenation and condensation reactions. Under catalytic conditions, active radicals or ions combine, reducing edge defects and promoting carbon skeleton rearrangement and aromatisation, while preferentially consuming disordered structures such as small molecules, aliphatic chains, and oxygen-containing functional groups, and converting them into a conjugated carbon network [42]. The decrease in I_D/I_G is consistent with this selective consumption of disordered structures.

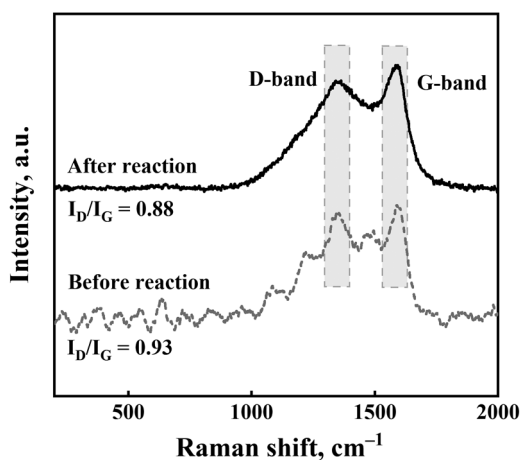


Fig. 8. Raman spectra of oil shale semi-coke before and after the reaction.

To further verify the occurrence of oxidative polymerisation, EA was performed on OSSC before and after the reaction. The results are summarised in Tables 5 and 6. Two key changes are evident from the EA data:

(1) Significant increase in the N/C ratio: The N/C atomic ratio increased from 0.076 to 0.120 (a rise of 57.89%), confirming the fixation of nitrogen from aniline into the OSSC solid phase, likely in the form of pyrrole- or pyridine-type nitrogen within a polymeric structure. This is closer to the N/C ratio of aniline ($\text{C}_6\text{H}_5\text{NH}_2$) and its polymer ($\text{N/C} \approx 0.167$).

(2) Pronounced decrease in the H/C ratio: The H/C ratio decreased from 1.945 to 0.744 (a decrease of 61.75%), which is a typical characteristic of oxidative polymerisation involving dehydrogenation or condensation to form unsaturated bonds and aromatic ring structures [43]. After the reaction, the H/C ratio (0.744) is closer to that of the fully oxidised state of polyaniline [$(\text{C}_6\text{H}_4\text{N})_n$] ($\text{H/C} = 0.667$) or the intermediate state [$(\text{C}_{24}\text{H}_{18}\text{N}_4)_n$] (0.75) [44] than to that of the monomer ($\text{H/C} = 1.167$).

Table 5. Elemental composition of oil shale semi-coke before and after the reaction, wt%

Element	C	N	O	S	H
Before reaction	5.499	0.492	6.041	1.033	0.891
After reaction	5.582	0.778	3.978	0.370	0.346

Table 6. Changes in the atomic ratios of oil shale semi-coke before and after the reaction

Atomic ratio	Before reaction	After reaction	Absolute change	Relative change
H/C	1.945	0.744	−1.201	−61.75%
N/C	0.076	0.120	+0.044	+57.89%
O/C	0.825	0.535	−0.290	−35.15%
S/C	0.070	0.026	−0.044	−62.86%

The decrease in the O/C ratio suggests that PS, acting primarily as an electron transfer agent, did not introduce oxygen into the solid phase but likely oxidised and decomposed oxygen-containing functional groups (e.g. $-\text{COOH}$ and $-\text{OH}$) in OSSC. The polymerisation process itself does not introduce additional oxygen and may even consume it. The reduction in the S/C ratio is attributed to the oxidation of sulphides in OSSC by PS, resulting in the dissolution of soluble sulphates.

Figure 9(a)–(c) presents the XPS spectra of OSSC before and after the reaction. The C 1s spectrum in Figure 9(a) shows that carbon atoms in OSSC primarily exist as C–C/C–H bonds, followed by C–O and C=O bonds, with carboxyl (–COOH) groups being the least abundant [45]. After the reaction, the peak at 285.9 eV (C–C/C–H) intensified, and the carboxyl peak (originally at 289.0 eV) shifted towards the carbonyl position (288.1 eV), indicating the transformation of oxygen-containing groups, including the decarboxylation of –COOH to C=O, consistent with the decreased oxygen content determined by EA.

The N 1s spectrum (Fig. 9b) shows notable changes. In pristine OSSC, nitrogen exists mainly as pyridine-N (398.40 eV) and pyrrole-N (400.72 eV) within macromolecular structures [40, 41], with a minor contribution from protonated pyridine-N (402.77 eV). After the reaction, a new peak emerged at 399.59 eV, the peak at 400.5 eV intensified, and the protonated pyridine-N peak shifted to 401.72 eV. This pattern closely resembles the N 1s spectrum of polyaniline (PANI), which exhibits characteristic peaks at approximately 398.8, 399.5, 400.4, and 401.6 eV [46]. This similarity confirms that aniline underwent oxidative polymerisation on the OSSC surface, forming protonated imine-based polymers. The O 1s spectrum (Fig. 9c) showed no major changes after the reaction, with only slight shifts to higher binding energies, indicating a slight decrease in electron density around oxygen atoms.

The normalised FTIR spectra (Fig. 9d) provide additional evidence. Peaks at 3695 and 3622 cm^{-1} are attributed to O–H stretching vibrations, which may originate from water adsorbed on the OSSC surface or hydroxyl groups within the structure [17]. The peak at 1618 cm^{-1} corresponds to the surface C=O double bond stretching vibration peak, whereas the peaks near 1050 and 1040 cm^{-1} correspond to Si–O bond vibration absorption [33, 45]. The peaks at 2925 and 2853 cm^{-1} correspond to C–H stretching vibrations in CH_3/CH_2 [47]. Notably, in the 1690–1500 cm^{-1} region, corresponding to double-bond stretching vibrations, the post-reaction OSSC exhibits a significant increase in the number of small, sharp peaks compared with the pre-reaction state, which typically correspond to vibrations of groups such as C=C, C=N, N=N, and benzene ring skeletons. Overall, the positions of the newly introduced characteristic peaks align with the spectral trends observed for PANI spectra [48, 49].

In conclusion, the characterisation results from Raman spectroscopy, EA, XPS, and FTIR provide a coherent chain of evidence. The observed increase in structural order, nitrogen fixation accompanied by significant dehydrogenation, the generation of polyaniline-like nitrogen species alongside oxygen-group transformation, and the appearance of characteristic double-bond and aromatic vibrations collectively prove that aniline undergoes oxidative polymerisation on the OSSC catalyst, resulting in the formation of nitrogen-containing polymeric composites.

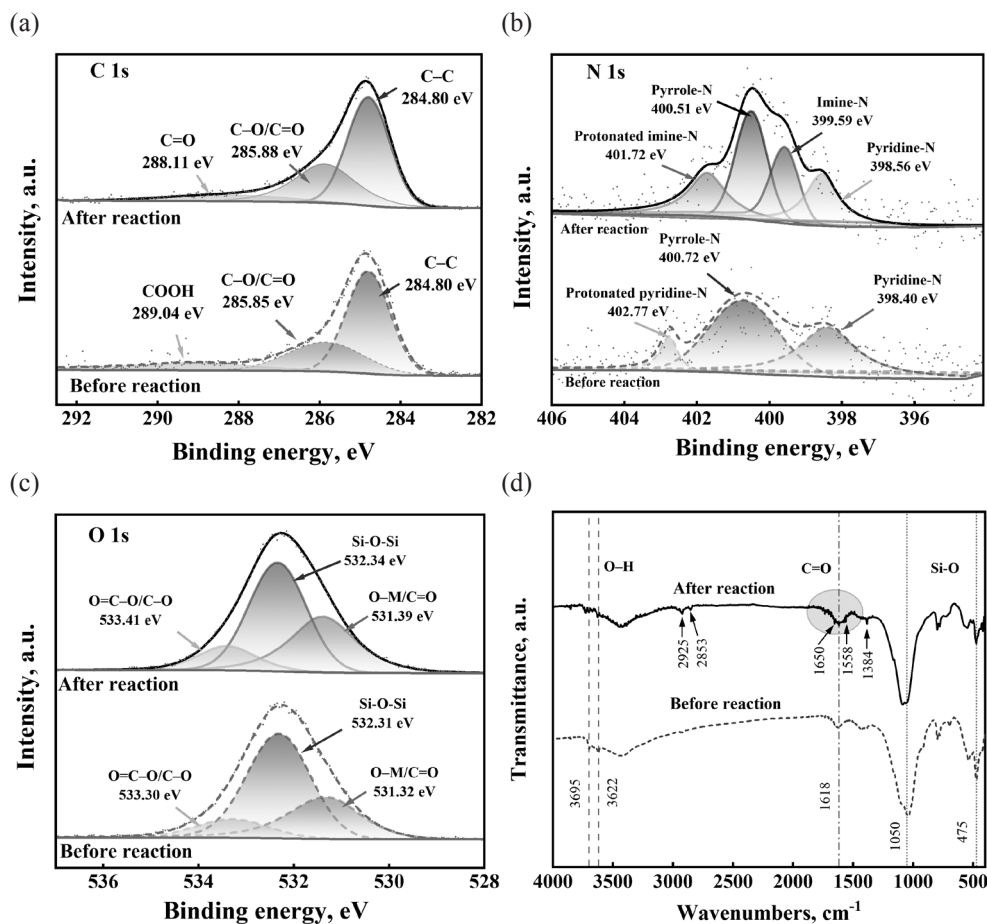


Fig. 9. X-ray photoelectron spectroscopy spectra of oil shale semi-coke before and after the reaction: (a) C 1s spectrum; (b) N 1s spectrum; (c) O 1s spectrum; and (d) Fourier transform infrared spectroscopy images of oil shale semi-coke before and after the reaction.

4.3. Evolution of inorganic components and iron speciation

To investigate whether the inorganic components in OSSC participate in the reaction, XRD and XRF analyses were conducted before and after the reaction. XRD (Fig. 10(a)) indicated that the inorganic components of OSSC primarily consist of SiO_2 , Al_2O_3 , and Fe_2O_3 , and the XRF results (Table 7) confirmed this, with no significant changes observed before and after the reaction, indicating good overall chemical stability. This result directly corroborates the conclusion from the TG-DTG analysis in Section 4.1: the very high residual mass percentage of OSSC before and after the reaction is precisely due to these chemically stable inorganic mineral components.

However, the XRD curve after the reaction was flatter than before, possibly due to amorphous reaction products covering the OSSC surface. The XRF results show the largest increase in Fe_2O_3 content (+30.86%), which may be due to the oxidation of Fe^{2+} in OSSC by PS to Fe^{3+} (i.e. Fe_2O_3), suggesting that iron may catalyse the production of active free radicals ($\text{SO}_4^{\bullet-}$) through valence state changes, participating in the initiation step of aniline oxidation polymerisation. The increase in K_2O may be due to residual $\text{K}_2\text{S}_2\text{O}_8$, while fluctuations in TiO_2 may be related to surface adsorption. The decrease in other components may be associated with dissolution in an acidic environment and coverage by polymerisation products.

The Fe 2p spectrum obtained via XPS (Fig. 10(b)) was used to investigate changes in the valence state of Fe before and after the reaction. After the reaction, the characteristic peaks at 711.28 eV ($\text{Fe}^{3+} 2p_{3/2}$), 714.87 eV (Fe^{3+} satellite peak), and 724.51 eV ($\text{Fe}^{3+} 2p_{1/2}$) correspond to the pre-reaction peaks at 711.67, 717.17, and 725.16 eV, respectively. The peak at 729.69 eV before the reaction may be a surface defect or coordination peak of Fe^{3+} in OSSC. After the reaction, this peak shifted to 727.65 eV, which is more consistent with the characteristics of Fe-N-C materials [50], possibly indicating the formation of coordination bonds between Fe^{3+} and the aniline polymer. After the reaction, all characteristic peaks shifted to lower binding energies, indicating an increase in electron density around iron. This is attributed to the formation of coordination bonds between Fe^{3+} and electron-rich groups (such as $-\text{N}=$ or $-\text{NH}-$) from the intermediate products of the Fe^{3+} -aniline reaction. Nitrogen acts as an electron donor, supplying electrons to the vacant orbitals of Fe^{3+} , ultimately promoting the formation of Fe-N-C coordination bonds.

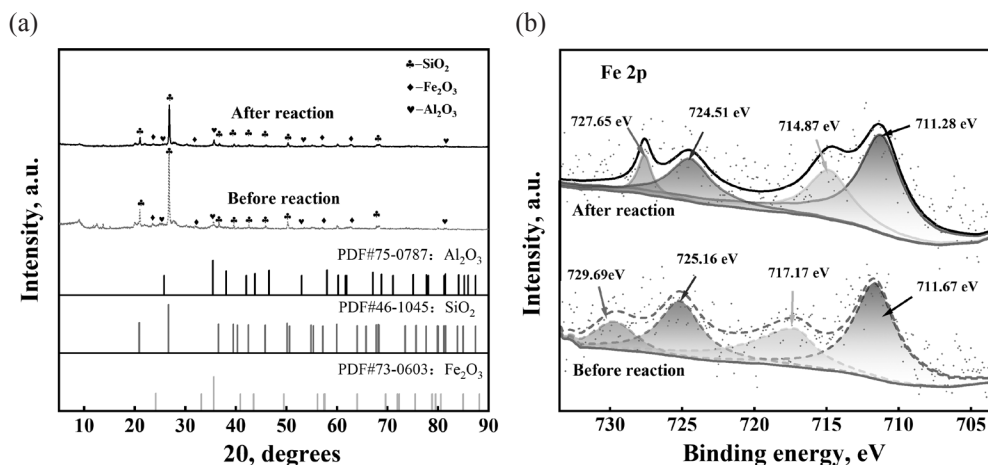


Fig. 10. (a) X-ray diffraction patterns; (b) high-resolution X-ray photoelectron spectroscopy spectra of Fe 2p for oil shale semi-coke before and after the reaction.

Table 7. Chemical composition of oil shale semi-coke before and after the reaction, wt%

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	SO ₃	TiO ₂	Other
Before reaction	61.00	23.50	8.10	1.39	1.35	1.25	1.23	2.18
After reaction	60.60	21.80	10.60	1.59	1.17	1.08	1.56	1.60
Change rate, %	−0.66	−7.23	+30.86	+14.39	−13.33	−13.60	+26.83	−26.61

4.4. Preliminary reaction mechanism and pathways

Free radical quenching experiments were conducted using 0.1 mol/L solutions of methanol, tert-butanol, *p*-benzoquinone, and furfuryl alcohol as radical inhibitors for SO₄•[−], •OH, O₂•[−], and ¹O₂ in the system. The results are shown in Figure 11. Under the high-temperature conditions (80 °C), the group treated with furfuryl alcohol showed the least effect, while the group treated with *p*-benzoquinone showed the greatest effect, followed by methanol. This suggests that under acidic and high-temperature conditions, O₂•[−] plays a primary role in the reaction, while •OH and SO₄•[−] may also contribute to the degradation of aniline, possibly due to the decomposition of potassium persulphate under high-temperature conditions. However, since the radical inhibitors could not completely inhibit aniline removal by OSSC, it indicates that the system involves more than just radical pathways.

The characterisation results showed that the Fe₂O₃ content in OSSC underwent significant changes after the reaction. The Fe 2p energy spectrum confirmed the formation of new Fe-N-C bonds, indicating that the inorganic components of OSSC participated in the process. Elemental analysis showed an increase in carbon content, while FTIR, XPS, Raman spectroscopy, and previous studies [22] collectively indicated that pollutant removal in the OSSC/PS system is achieved through a dual mechanism involving both radical and non-radical pathways. GC-MS analysis of the post-reaction water samples detected seven organic compounds (excluding the chloroform extractant), including 2-octanamine, cyclooct-4-en-1-ol, 8-iodo-, acetate, acetone, butane, 2-chloro-2-methyl-, guanidine, 4-penten-2-ol, and hydrogen chloride (only the first matching item is listed). The detection of these newly formed low-molecular-weight and heterocyclic compounds provides direct evidence for the introduction of organic components with lower thermal stability, as inferred from the TG-DTG analysis. Importantly, no aniline peak was observed (retention time typically 3–5 min; molecular weight 93 amu), confirming its effective conversion and degradation. The absence of polymeric products may be attributed to secondary filtration during

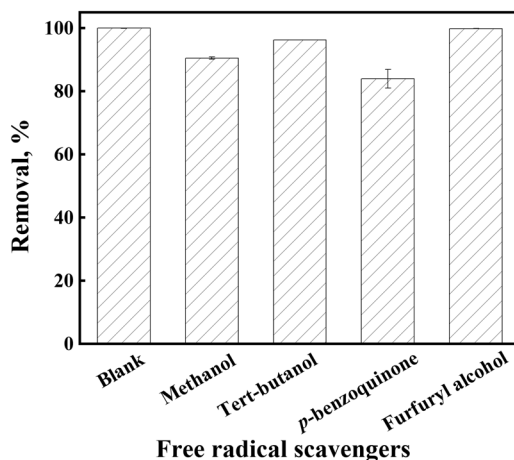
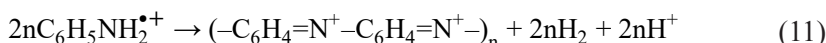
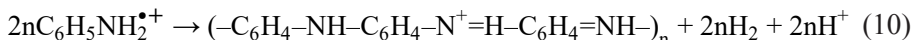
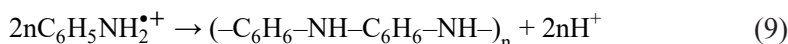
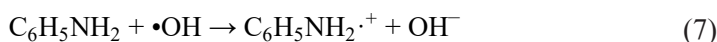
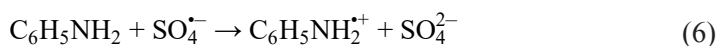
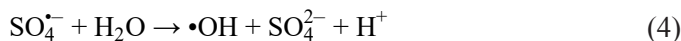
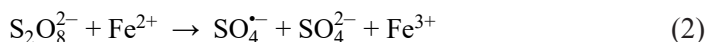


Fig. 11. Effect of free radical scavengers on the OSSC/PS system.

water characterisation and the primary loading of products onto OSSC. However, the detection of oxygen- and nitrogen-containing heterocyclic compounds, multi-functional amino- and hydroxy compounds, and guanidine derivatives indicates the presence of amino oxidation-condensation reactions. The simultaneous detection of low-molecular-weight substances (e.g. acetone) confirms the coexistence of ring-opening mineralisation processes and polymerisation reactions.

Based on the characterisation results obtained for the degradation of aniline by PS activated with OSSC, the reaction mechanism can be summarised as the following synergistic processes. First, the low-valent iron (Fe^{2+}) in OSSC activates PS ($\text{S}_2\text{O}_8^{2-}$) to produce sulphate radicals ($\text{SO}_4^{\bullet-}$) and hydroxyl radicals ($\bullet\text{OH}$), while under acidic and thermal conditions, PS spontaneously decomposes to generate superoxide radicals ($\text{O}_2^{\bullet-}$). These reactive oxygen species attack aniline molecules to form cationic free radicals ($\text{C}_6\text{H}_5\text{NH}_2^{\bullet+}$), triggering dehydrogenation and coupling reactions. Aniline monomers undergo stepwise polymerisation through head-to-tail condensation to form poly(aniline) chains. This process is accompanied by significant dehydrogenation (elemental analysis shows that the H/C ratio decreases from 1.94 to 0.74) and nitrogen atom retention (the N/C ratio increases by 55.8%), resulting in a polymer with a structure primarily composed of protonated imines and phenyl amines. Based on the described reaction mechanism, the involved chemical equations are summarised as follows: Eqs (2)–(5) represent the activation of PS to generate radicals; Eqs (6)–(8) correspond to the formation and initiation of aniline radicals; and Eqs (9)–(11) describe the stepwise polymerisation of aniline radicals, with head-to-tail coupling corresponding to Eq. (9), head-to-head coupling to Eq. (10), and tail-to-tail coupling to Eq. (11).



The polymerisation products are fixed to the OSSC carrier via two pathways. First, the polyaniline chains are embedded within the mesoporous structure of the OSSC; second, the Fe^{3+} generated by oxidation in the OSSC forms Fe-N coordination bonds with the imine nitrogen of the polyaniline (as evidenced by a decrease in the binding energy of Fe 2p in XPS and the appearance of a characteristic Fe-N-C peak). This system simultaneously involves both radical pathways (direct oxidation by $\text{SO}_4^{\bullet-}/\bullet\text{OH}/\text{O}_2^{\bullet-}$) and non-radical pathways (electron transfer mediated by Fe^{3+}), which synergistically achieve the efficient conversion and fixation of aniline, ultimately forming a ‘OSSC-polyaniline’ composite, as shown in Figure 12.

The oxidative polymerisation pathway revealed in this study is not an isolated case. Recent research indicates that in PS-based advanced oxidation systems, the transformation and immobilisation of pollutants (e.g. phenols and aniline) via non-radical or radical-mediated polymerisation is a promising strategy for carbon resource recovery. For instance, biochar can drive electron transfer and induce phenolic polymerisation through the co-activation of pollutants and PS, achieving an electron utilisation efficiency as high as 182% [51]; heat-activated PS systems can efficiently convert aromatic contaminants

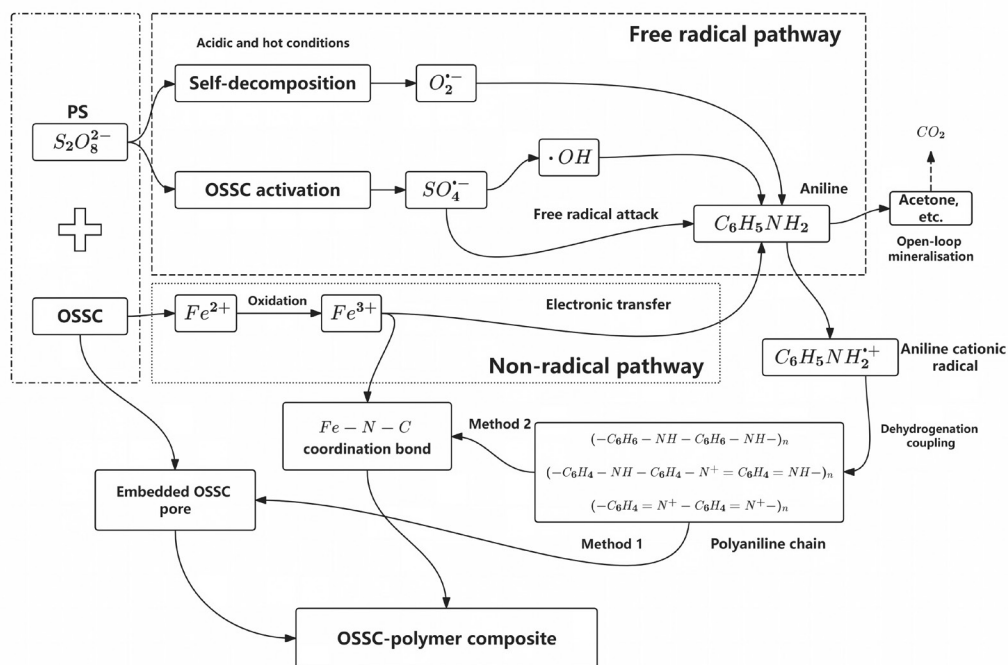


Fig. 12. Mechanism diagram of the OSSC/PS treatment of aniline.

into separable solid polymers, significantly reducing oxidant consumption and mineralisation-related carbon emissions [52]. These studies collectively demonstrate that the oxidative polymerisation pathway can effectively achieve pollutant removal, immobilisation, and carbon resource recovery. This study, utilising OSSC to activate PS for aniline wastewater treatment, further confirms the feasibility of this pathway and provides a concrete case for the ‘waste-treats-waste’ approach and the valorisation of solid waste.

5. Conclusion

This paper thoroughly investigates the feasibility of using oil shale semi-coke as a catalyst for wastewater treatment and the mechanism of activated persulphate degradation of aniline. The study found that the degradation efficiency of aniline was significantly improved under the synergistic action of OSSC and PS. Through orthogonal experiments, the optimal reaction conditions were determined to be as follows: $T = 80\text{ }^{\circ}\text{C}$, $PS = 7.5\text{ mM}$, $OSSC = 5\text{ g/L}$, $pH = 3$, and $t = 60\text{ min}$, at which point the aniline removal can reach 100%. Mechanistic analysis indicates that low-valent iron (Fe^{2+}) in OSSC can activate PS to generate sulphate radicals ($SO_4^{\bullet-}$) and hydroxyl radicals ($\bullet OH$), while PS spontaneously pyrolyses under acidic and thermal conditions to produce superoxide radicals ($O_2^{\bullet-}$). These reactive oxygen species

attack aniline molecules, triggering dehydrogenation and coupling reactions that polymerise aniline monomers into poly(aniline) chains, accompanied by significant dehydrogenation and nitrogen atom retention, ultimately forming an OSSC-poly(aniline) composite. This system combines both radical and non-radical pathways, which synergistically achieve efficient conversion and fixation of aniline. This study provides new insights into the resource utilisation of OSSC and the treatment of aniline-containing wastewater, while also offering valuable references for the development of advanced oxidation processes.

Data availability statement

Data will be made available upon request.

Acknowledgements

The project was supported by the Science and Technology research project of Liaoning Provincial Department of Education (project No. JYTMS20231460) and the Talent Scientific Research Fund of LNPU (project No. 2020XJL-015). The publication costs of this article were partially covered by the Estonian Academy of Sciences.

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Foto: Aleksandra Kurvits-Vahter

ANDRES SIIRDE: nearly two decades with Oil Shale

The approaching departure of Andres Siirde as Editor-in-Chief of *Oil Shale* marks the end of an important chapter in the history of the journal and Estonian oil shale research. He has been part of the journal's editorial leadership team for almost 20 years, first serving as Deputy Editor-in-Chief from 2008 to 2018, and then as Editor-in-Chief from 2019 to the present. During this time, he has not only helped the journal maintain its position in the fields of oil shale geology, chemistry, energy, technology and environmental impacts, but also helped to strengthen it.

As Editor-in-Chief, he has consistently upheld the scientific quality of published articles and promoted a balanced approach to the topics addressed. Under his leadership, *Oil Shale* has continued to serve as an independent international scientific journal dedicated to oil shale research, even as the role of oil shale in Estonia's energy sector and society has undergone far-reaching changes and been subject to intense debate. Thanks to Andres, the journal has preserved continuity in knowledge and experience, and he has consistently supported opportunities for young researchers to publish their work.

At editorial board meetings and in private conversations, Andres Siirde has repeatedly emphasised the need to address the present and future use of Estonian oil shale on a scientific basis. His conviction is aptly summarised by the following statement: 'Oil shale can never be fully studied.' He regards oil shale not merely as an important domestic resource, but also as the foundation of the scientific, technological, and industrial expertise that has been developed in Estonia over many decades. He firmly advocates continuing research and development in the oil shale field, improving existing processes, reducing environmental impacts, and searching for higher-value applications for oil shale.

We would like to thank Andres Siirde for his long-standing, dedicated, and responsible work. His contributions to the development of the journal and the preservation of knowledge in the field of oil shale will endure long after he hands over his responsibilities as Editor-in-Chief.

We wish Andres continued energy, fresh ideas, and enduring enthusiasm in all his future endeavours!

Oliver Järvik and Alar Konist, members of the Editorial Board



PUBLISHER

Estonian Academy Publishers

Kohtu 6

10130 Tallinn, ESTONIA

info@eap.ee

www.eap.ee

EDITORIAL OFFICE

Kohtu 6

10130 Tallinn, ESTONIA

hedi.tonso@eap.ee

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Subscription information is available at www.eap.ee/subscription

Subscription orders should be sent to subscription@eap.ee

ISBN 0208 189X (print)
ISSN 1736-7492 (electronic)

