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[Research Note]

Preliminary Analysis of Oil Shale Obtained from Kalynkara in Kazakhstan

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Oil shale obtained from Kalynkara in Kazakhstan was investigated by powder XRD, XRF, SEM, TG-DTA, and EA. The XRD profiles indicated that the oil shale contained quartz (major component), $CaSO_4 \cdot 2H_2O$, and $Mg_4Al_2(OH)_{12}CO_2 \cdot H_2O$ as minerals. The amount of organic matter in the oil shale was determined by TG-DTA and was approximately 19 wt% based on the weight loss in the temperature range of 473-823 K. Moreover, the H/C ratio determined by EA and TG-DTA was 0.86, indicating that the structure of the organic matter was similar to that of coal. We attempted to extract the organic matter from the oil shale in decalin at 373-623 K, but no significant amount of products was obtained.

Keywords

Oil shale, Kazakhstan, Thermal analysis, Elemental analysis, Hydrogen/Carbon ratio

1. Introduction

Alternative carbon resources to petroleum have been actively researched, because the price of petroleum has risen in recent years, and oil shale is one of the promising carbon resources and contains 5-81 wt% organic carbons[1)~3)]. However, the organic compounds were hardly extracted from the shale using a solvent, therefore, a retorting method has been generally used for the extraction of the oil components. Additionally, the physical and chemical properties between the shale ores are obviously different at the mining areas[1)]. As examples, the amount of included organic compounds, the ratio of hydrogen to carbon, and the amount of elements such as nitrogen, sulfur, and phosphorus affect the fuel quality; especially, the S, N, and P compounds can possibly form environmental pollutants when the oil shale is burned. Moreover, the amount of organic compounds and their decomposition temperature also affect the production efficiency. Therefore, in order to obtain fundamental analysis data, many researchers have investigated the regional characteristics of the oil shale by instrumental analyses[4)~20)]; Such oil shale data from China[15),16),18),20)], India[19)], Israel[8)], Jordan[9),12)], Morocco[13)], Nigeria[14)], Thailand[5)], Turkey[10),11)], and the United States[4)~7),17)] have been reported.

Recently, we investigated the gasification of the organic compounds incorporated in the oil shale obtained from the Kenderlyk deposit in Eastern Kazakhstan[21)]. In this study, we conducted a preliminary analysis of the oil shale obtained from Kalynkara in the Kenderlyk deposit using thermal, elemental, and phase analyses in addition to surface observations by a scanning electron microscope.

2. Experimental

All analyses were performed using ground oil shale. The particle sizes of the powder sample determined by the scanning electron microscopy (SEM) photograph were not more than 100 μm in diameter.

2. 1. Thermal Analysis

Thermogravimetry (TG) and differential thermal analysis (DTA) of the oil shale were performed using a Shimadzu DTG-60 thermal analyzer. The measurements were done in a dry air atmosphere in the temperature range from ambient temperature to 1073 K. The rate of the temperature increase was 10 K min^{-1}.

2. 2. Elemental Analysis

The elemental analysis (CHN analysis) for the organic components in the oil shale was performed using a Thermo Fisher Scientific K.K., FLASH EA1112.

The amount of inorganic compounds in the shale was determined by an X-ray fluorescent analysis (XRF) using a Spectris Co., Ltd., PW2400. The shale was calcined at 673 K for 1 h in air to remove any volatile

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matter before the measurement. A self-supported disk (20-mm diameter) consisting of the shale and cellulose mixture (total = 0.250 g, oil shale : cellulose = 1 : 1 by weight) was prepared for the XRF measurement. The amount of each component was calculated by UniQuant™ 4 (Standardless Quantitative Analysis), and total amount was normalized to 100 %.

2. 3. XRD Measurements

An X-ray diffractometer (XRD, Rigaku Corp., Ultima III) was used for the determination of the crystal phase of the shale. The shale was analyzed under the following conditions: CuKα line (λ = 0.15406 nm), 40 kV, 40 mA, sweep angle (2θ) = 10-60°, and scan rate = 4° min^{-1}.

2. 4. Scanning Electron Microscopy

The surface morphology of the shale was observed using a high resolution SEM equipped with a field-emission electron gun (Hitachi High-Technologies Corp., S-4100). Before the measurement, the sample was coated with a Pd-Pt alloy in order to afford it conductivity. The measurement was carried out under the following conditions: accelerating voltage = 15 kV, working distance = 15 mm.

3. Results and Discussion

Figure 1 shows the TG-DTA analysis results of the oil shale. The weight loss proceeded through three stages. First, the weight loss between r.t. and 473 K was observed with an endothermic reaction at 387 K, and that value was 8.60 wt%. This weight-loss was assigned to the desorption of water, and the same behavior was reported in the literature[20]. In the temperature range between 473 K and 823 K, an exothermic reaction was observed with a 19.1 % weight loss as the second stage. This weight loss was attributable to the combustion of the organic compounds in the oil shale. The weight loss in the temperature range from 823 to 1973 K was 5.7 wt%, suggesting the decomposition of inorganic compounds.

We conducted an elemental analysis (CHN analysis) of the oil shale in order to confirm the carbon and hydrogen contents in the shale, and the observed values (wt%) of C, H, and N were 10.38, 1.71 and 0.65, respectively. Meanwhile, the TG-DTA analysis results indicated that 8.60 wt% of the sample (0.96 wt% as hydrogen) was water, and after the calibration, the C : H : N molar ratio was 1.0 : 0.86 : 0.05.

Table 1 shows the results of the XRF analysis of the oil shale. The main component of the oil shale was silicon, indicating that SiO_2 or a silicate compound was contained in the shale. The XRF data also indicated the existence of sulfur compounds in the shale. The molar ratio of Ca/S was 0.82 based on the XRF measurement, and this value strongly suggested that the sulfur compound was $CaSO_4$. This speculation was consistent with the following results: A large amount of sulfur remained in the shale despite the sample being calcined at 673 K, because the decomposition temperature of $CaSO_4$ is greater than 1273 K. Apart from these compounds, the XRF results suggested that the shale contained aluminum and iron compounds, but we did not determine any other compounds from the XRF measurement results.

The compounds in the shale were determined by XRD. **Figure 2** displays the XRD profiles of the oil shale (a) before and (b) after its heat treatment at 673 K

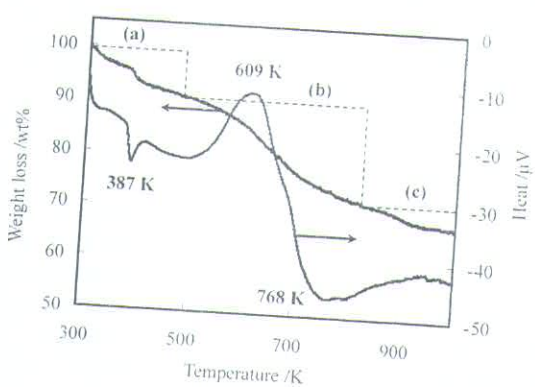
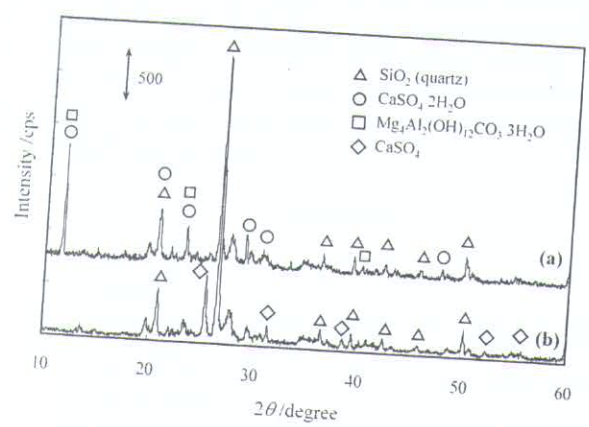


Fig. 1 Thermal Analysis Results of Oil Shale



(a) Without any treatment and (b) drying at 673 K for 1 h.

Fig. 2 XRD Profile of Oil Shale

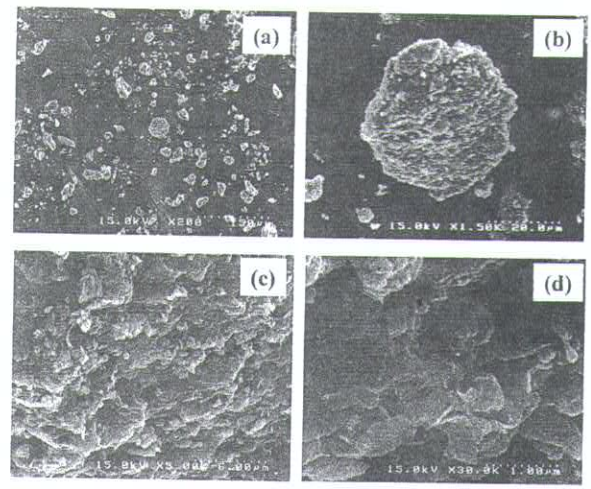
Table 1 XRF Analysis of Oil Shale

Major components [wt%]									
Na_2O	MgO	Al_2O_3	SiO_2	S	P	K_2O	CaO	Fe_2O_3	TiO_2
1.9	2.8	13.4	54.9	5.4	0.5	2.4	7.8	4.9	0.6

for 1 h. The weight loss of the oil shale by the heat treatment was 21.4 wt%. This value was the nearly equal to the weight loss (22.5 wt%) in the temperature range from r.t. to 823 K obtained by the TG-DTA analysis. Based on the XRF analysis, we compared the peak data of the diffraction profile to those of Si compounds in the ICDD database. The peaks observed at $2\theta = 20.84$, 26.61, 36.49, 39.48, 50.09, and 59.93° were in good agreement with both the diffraction angles and peak intensities described in the standard data of quartz (SiO_2, No. 041-1045). Subsequently, the peaks in the XRD profile of the oil shale before the calcination were verified to the standard data of sulfur compounds. The matching results indicated the existence of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$); the major diffraction peaks at $2\theta = 11.63$, 23.35, 29.07, 31.11, 33.35, and 43.33° were in good agreement with those in the standard data (No. 033-0311), however, the relative intensities of one major peak (11.63°) did not match these described in the standard data. This fact implied that the diffraction peak of other materials overlapped the major peak, and therefore, we searched for a compound that has a diffraction peak at 11.6°. As a result, we determined the compound to Mg–Al double hydroxide $Mg_4Al_2(OH)_{12}CO_2 \cdot H_2O$, because the observed diffraction peaks ($2\theta = 11.63$, 23.47, 49.91°) well matched the peaks reported in the ICDD database (No. 051-1528). After the heat treatment, the diffraction profile dramatically changed; the strong diffraction peak at 11.6° disappeared. This change was attributable to the dehydration of $CaSO_4 \cdot 2H_2O$ to anhydrous $CaSO_4$, resulting from the fact that the peaks derived from $CaSO_4 \cdot 2H_2O$ disappeared and new peaks derived from anhydrous $CaSO_4$ appeared at 25.44, 31.37, 38.66, 52.27, and 55.72°. Moreover, the diffraction peaks derived from $Mg_4Al_2(OH)_{12}CO_2 \cdot H_2O$ also disappeared due to its decomposition by dehydration. Many researchers have reported that calcium exists as calcite ($CaCO_3$)[9),12)~14),17),18),20)]; however, the oil shale obtained from Kazakhstan did not contain a significant amount of calcite. The characteristic diffraction peaks of clay minerals (kaolinite, montmorillonite, illite, and muscovite) and dolomite, which were also reported as typical components of oil shale by these researchers, were not observed in the XRD profiles.

Figure 3 shows the SEM photographs of the powdery oil shale. The particles had a wide particle-size distribution and their shapes were indefinite (a), because the powdery shale was produced by crushing the original shale. The characteristic sheet-like structures were observed in the magnified photograph ((c)-(d)) of the shale.

The solvent extraction of organic matter from the Jordan oil shale using ultrasonic waves was reported by Matouq *et al.*[22]. We tried to extract the organic compounds from the oil shale (5.0 g) with decalin (40 mL)



Magnification: (a) × 200, (b) × 1500, (c) × 5000, and (d) × 30,000.

Fig. 3 SEM Photographs of Oil Shale after Heat Treatment at 673 K for 1 h

at 373-623 K for 2 h, but no significant amounts of organic compounds were detected by gas chromatography. Moreover, after the extraction, the TG-DTA analysis of the residual oil shale showed that most of the organic compounds remained in the oil shale (200-550 ℃, weight loss = 14 wt%). Those results indicated that the organic matter was similar to that of coal, which has low solubility and a high decomposition temperature. Although we cannot extract oil from the Kazakhstan oil shale by the solvent extraction, some useful information was obtained by the instrumental analyses.

In summary, the content of the organic matter in the Kazakhstan oil shale was nearly equal to a typical oil shale, whereas the H/C ratio was relatively low[2]. Therefore, the gasification with steam was considered to be a promising process for the utilization of the Kazakhstan oil shale.

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要　旨

カザフスタン，カリンカラ産オイルシェールの組成分析

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カザフスタン，カリンカラ産のオイルシェールについて，粉末X線回折法（XRD），蛍光X線分析（XRF），走査型電子顕微鏡（SEM），熱重量-示差熱測定（TG-DTA），および元素分析（EA）により分析した。XRDの回折パターンより，オイルシェールは，鉱物として，石英，$CaSO_4 \cdot 2H_2O$，および$Mg_4Al_2(OH)_{12}CO_2 \cdot H_2O$を含んでいることが分かった。TG-DTAの473～823 Kの間の重量減少に基づいて算出されたオイルシェール中の有機物は約19％であった。さらに，EAとTG-DTAから求めたH/C比は0.86であり，これは含まれる有機物が石炭のそれに近いことを示していた。我々は，373～623 Kにおいて，デカリンを用いてオイルシェールからの有機物の抽出を試みたが，有意な量の生成物は得られなかった。