[Technical Report]

Screening Method for Oil Shale Samples for Fischer Assay

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The oil shale deposit survey requires testing of a number of oil shale samples. However, the Fischer assay can process only 4-5 samples a day, so the number of samples should be limited. Hence a quick method to screen the samples for the Fischer assay test is required.

The automatic micro carbon residue (MCR) test is proposed as a quick and simple screening method which requires only 100 mg of sample. The MCR test, as specified in JIS K 2270 (modified ISO 10370), can predict the weight loss of oil shale samples in the Fischer assay. Although the MCR test provides only data on the weight loss of oil shale, 12 samples can be processed in 2-3 h, the structure and control are simple, the cost is relatively low, and the equipment is easy to use. There is a definite correlation between the upper limit of oil yield from oil shale and the weight loss of oil shale, so the MCR test can facilitate the rapid screening of a large number of oil shale samples.

Keywords

Oil shale, Kerogen, Screening method, Carbon residue, Micro method, Fischer assay

1. Introduction

The first step in the development of oil shale deposits is a quality and size survey of the deposit using bore holes. The technique involves drilling many wells, sampling the core at different depths, and determining the oil content in each sample. A very large number of samples is collected by such a survey, so a rapid evaluation method for oil shale samples is required.

Up to now, the quality of oil shale has been determined mainly by the Fischer assay. This assay is carried out by heating 80-100 g of sample in a specific temperature pattern determined by USBM No. 5239. Although the Fischer assay test requires a large amount of sample, the shale oil sample can actually be recovered. Therefore, the Fischer assay is still regarded as the standard method for quality evaluation of oil shale. Many other oil shale evaluation methods have been reported including a thermal decomposition method by Rock Eval[1], the Gray–King assay[2] which requires only a few grams of samples, thermogravimetric analysis[3], and a method using ^{13}C-NMR (nuclear magnetic resonance)[4], but none of these has become a standard method.

The Fischer assay requires about 2 h to process each sample, so one apparatus can process only 4-5 samples per day. It is not unusual to collect more than 100 samples from a single well, so much equipment is required to carry out rapid evaluation. Therefore, the survey stage requires a considerable amount of investment. Oil shale is anticipated to provide energy resources in non-oil producing countries which cannot import adequate supplies of crude oil. Most of these countries will not be able to afford many Fischer assay devices. Therefore, a rapid and economical evaluation method which does not require much capital investment would be very useful.

The present study investigated a rapid evaluation method for oil shale using a micro carbon residue (MCR) tester for the Conradson carbon residue to identify samples suitable for Fischer assay.

2. Materials and Methods

2. 1. Test Device

An MCR tester (ACR-M2; Tanaka Scientific Ltd., Tokyo) specified for the JIS K 2270 micro method (modified ISO 10370) was selected. This tester requires a source of high-pressure nitrogen at more than 0.2 MPa and a flow rate of 600 ml/min. A sample holder is attached to the device and the holder can accommodate up to 12 sample tubes at the same time (**Fig. 1**). The measurement conditions are prescribed in the JIS as follows (**Table 1**): temperature increase in the furnace to 500°C over 40 min, steady temperature for 15

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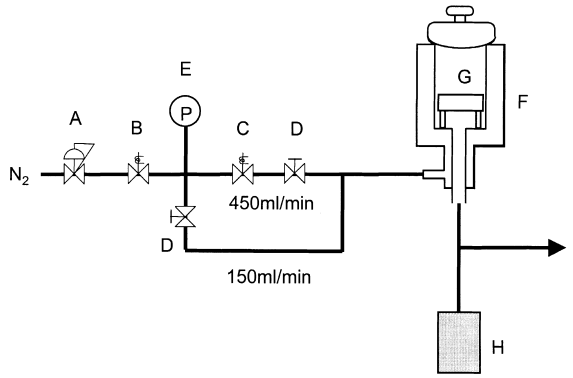
min, when the assay is started, purge in the furnace by opening the solenoid valve C to introduce nitrogen gas at 600 m*l*/min, then close the valve C after 10 min, and finally sweep the furnace with nitrogen gas at 150 m*l*/min (Pattern 1). The measurement is fully automatic and the only operation required is to set up the sample holder and press a button. This study also investigated two other sets of measurement conditions, *i.e.*, temperature increase to 500°C over 50 min, steady temperature for 20 min, followed by sweep gas flow rate at 600 m*l*/min, which is the same condition as for the Fischer assay (Pattern 2); and the same temperature condition as Pattern 2 with the same gas flow rate pattern as Pattern 1 (Pattern 3).

2. 2. Oil Shale Samples

Six oil shale samples with different Fischer assay oil yields were selected from the world-wide oil shale samples collected in a research program on oil shale by the Japan National Oil Corporation and our in-house research project (**Table 2**). The oil contents and the weight losses of all oil shale samples had been determined by an automatic Fischer assay device (Model MRF-81W; Ryomei Giken Co., Ltd.). For the MCR test, about 100 mg of sample was transferred to a sample tube for which the tare weight had been recorded with 0.1 mg accuracy and duplicate tubes were prepared for each of the samples. Six samples, 12 tubes in total, were set in the sample holder and the assay was carried out. After the assay was completed, the sample holder was cooled to room temperature and the weight loss was determined by measuring the final weight of each sample tube.



A: Pressure regulator. B, C: Solenoid valve. D: Needle valve.
E: Pressure gauge. F: Furnace. G: Sample holder. H: Trap.

Fig. 1 Schematic Diagram of the MCR Tester

3. Results and Discussion

3. 1. Correlation between the Weight Loss of Oil Shale and Oil Yield

Retorting of oil shale produces water and gas as well as oil, and the relative amounts depend on the quality of the oil shale. The weight loss reflects the total amounts of oil, gas and water. The production of gas and water is inevitable, so the oil yield is always lower than the weight loss. Our previous Fischer assay[5] tests showed that the oil yield is limited to the level of the weight loss (**Fig. 2**) and the oil yields are distributed under the line shown in **Fig. 2**. The plot shows that the further the dot is from the line, the less oil yield is obtained against weight loss. The plots on the line represent samples containing kerogen with low aromaticity. These results indicate that the upper limit of the oil yield can be predicted by measuring the weight loss, even if the properties of the oil shale are unknown.

Using this correlation, borehole samples can be screened out with lower weight loss than a value decided in advance, which can be selected to allow economical shale oil production.

Table 2 Recovery of Oil Shales by Fischer Assay

Sample	Recovery [wt%]			
	Oil	Water	Spent shale	Wt. loss
A	29.1	3.1	60.9	39.1
B	11.3	3.2	79.9	20.1
C	10.3	0.0	85.0	15.0
D	5.1	2.8	88.8	11.2
E	2.4	3.5	91.4	8.6
F	0.0	3.3	95.5	4.5

Table 1 The Conditions for the MCR Test

		Fischer assay	Pattern 1	Pattern 2	Pattern 3
Initial temp.	[°C]	rt[a)]	rt[a)]	rt[a)]	rt[a)]
Final temp.	[°C]	500	500	500	500
Heating period	[min]	50	40	50	50
Holding period	[min][b)]	20	15	20	20
Gas rate for purge	[m*l*/min][c)]	—	600	600	600
Gas rate for measurement	[m*l*/min]	500	150	600	150

a) Room temperature.
b) At final temperature.
c) First 10 min.

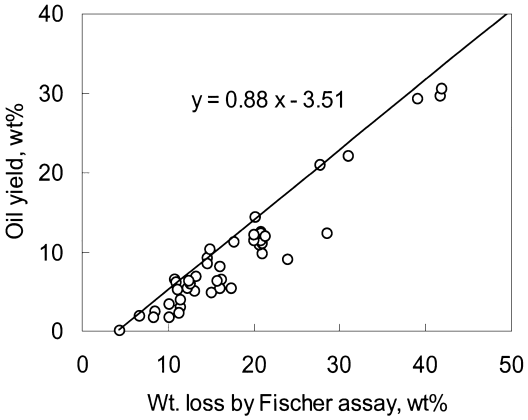


Fig. 2 Relationship between Weight Loss and Oil Yield Obtained by the Fischer Assay Test

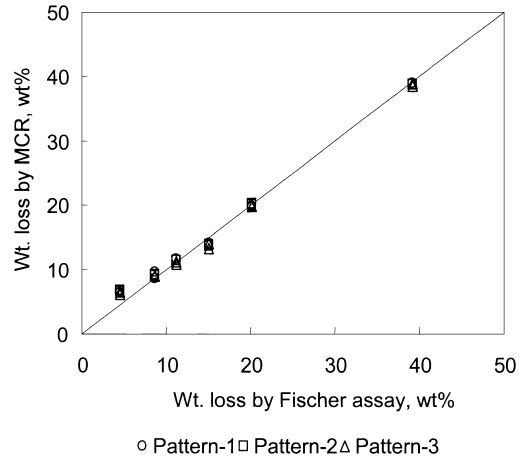


Fig. 3 Relationship between the Weight Losses Obtained by the Fischer Assay and MCR Test

3. 2. Measurement of the Weight Loss of Oil Shale by the MCR Tester

The weight losses determined by the Fischer assay of the samples used in this study were distributed in the range between 4.5 and 39.1%(w/w). **Figure 3** shows the relationship between the weight losses determined by the Fischer assay and by the MCR test. Six dots per sample, *i.e.*, the duplicate samples for 3 patterns, are plotted. All samples showed no differences between the patterns, so the reproducibility seems very good. The line in the figure indicates when both measurements of the weight loss are equal. The weight loss determined by the MCR test slightly exceeded the weight loss determined by the Fischer assay in samples at 4.5%(w/w), but the measurements of the weight loss were consistent for all other samples. Therefore, measuring the weight loss using an MCR tester could predict both the weight loss determined by the Fischer assay and the upper limit of oil yield.

The results indicate that the most suitable samples for Fischer assay show more than 9%(w/w) weight loss as measured by the MCR test, if the required oil yield is 5%(w/w) and more than 15%(w/w) weight loss for 10%(w/w) oil yield. The MCR tester has many advantages including the small sample size; ease of use with only a balance, nitrogen and electricity required; determination of the weight loss of 12 samples at once; automatic heat up and cool down; only 2-3 h for one cycle, so the test duration per sample is very short (10-12 min); and the MCR tester is inexpensive compared to the Fischer assay tester and other analytical devices. The MCR tester can easily be introduced in locations with poor infrastructure and facilitates rapid screening of core samples, so the efficiency of the survey is expected to improve dramatically by introducing this method.

4. Conclusion

A test method using only 100 mg of sample based on the automatic MCR tester allows the prediction of the weight loss of oil shale in the Fischer assay. The MCR test can determine 12 samples in 2-3 h, the structure and control are simple, and the tester is relatively inexpensive and easy to use. There is a definite correlation between the upper limit of oil yield and the weight loss of oil shale, so the MCR test facilitates the rapid screening of a large number of oil shale samples collected by an oil shale deposit survey to select the optimum samples for further analysis by the Fischer assay.

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要　　旨

フィッシャーアッセイ試験のためのオイルシェールのスクリーニング試験法

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オイルシェールのボーリング等による鉱床調査では多数の評価すべき試料が生じる。しかし，それらの中にはかなりの割合で低品位の試料も含まれる。従来のオイルシェール評価法ではこのような試料もフィッシャーアッセイ試験により評価を行っている。しかし，フィッシャーアッセイ試験は 1 試料あたり 2～3 時間を要するため，多数の試料を評価するためには，複数の装置または長時間を必要とする欠点がある。そのため，試料を短時間で多数処理できる評価法が望まれている。

本研究ではフィッシャーアッセイ試験のためのスクリーニング法として ISO 10370 を改良した JIS K 2270 に規定されている自動ミクロ残留炭素分試験装置の利用を検討した。本装置の特徴は，1 回あたり 2～3 時間の試験時間で 12 試料を試験することができ，装置の構造や操作も単純なことである。

本法により 100 mg 程度の試料でオイルシェールの重量減少が測定でき，さらにその値よりフィッシャーアッセイ試験における油収率の上限が推定できた。これにより低品位の試料を除外することが可能となった。

本法は多数のオイルシェールの迅速スクリーニング法として非常に有効であると考えられる。