



The chemistry of minerals obtained from the combustion of Jordanian oil shale

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Received 21 November 2003

Abstract

A characterization study was performed on the spent oil shale (oil shale ash) obtained from the combustion of Jordanian oil shale. This characterization utilized different analytical techniques. These include scanning electron microscope with energy dispersive spectrum analysis, X-ray fluorescence, X-ray diffraction and Qemscan. During the combustion process, minimal fragmentation was encountered since Jordanian oil shale contains large proportions of ash which maintain the original structure of the oil shale particle. Different analytical techniques confirmed that the dominant phase of minerals in the oil shale is calcite, which transforms, in parts, into anhydrite during combustion. Sulphur was found to be mainly of an organic source. This sulphur is combusted to produce SO₂ and then SO₃, which controls the sulphation reaction of the calcite. The dominant phase in the ash was the anhydrite in addition to the calcite, clays and calcium phosphate.

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1. Introduction

Jordan has limited energy resources such as crude oil or natural gas compared to its neighboring countries. However, oil shale is an important and unutilized energy source in the country. More than 50 billion tons of oil shale deposits are discovered in different areas especially in the middle and southern parts of the country [1].

Many investigations on the Jordanian oil shale have been done on process parameters in order to utilize oil shale. All of these studies focused on the organic part of the oil shale in order to utilize it as

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a substitute of oil. The parameters are mainly concerned with the thermal decomposition of oil shale under high temperatures and the effect of these variables on the yield of oil fraction. Results from these investigations indicated that the yield of liquid oil fractions is around 10 wt% and the sulphur content in the oil shale is around 3 wt% [2,3].

Extraction of kerogen from Jordanian oil shale using organic solvent was also studied. The results showed a weak solubility of organic matter contained in the matrix of the oil shale [4]. Shawaqfeh and Al-harahsheh [5] found that sulphur-containing solvents had a significant implication on solvation enhancement. A study of the chemical structure of obtained oil fraction was performed by Yorudas et al. [6], and Khraisha et al. [7]. The authors indicated that Jordanian shale oil is mainly aliphatic with a small amount of aromatic and olefinic compounds. Al-harahsheh et al. [8] investigated the structural distribution of sulphur in distillate fractions of obtained oil; the structures of sulphur containing compound were identified to be basically of naphthene rings in different combinations with aliphatic alkyls.

Although the ash proportions of Jordanian oil shale is relatively high (around 50%), there is no available literature on the chemistry and transformation of Jordanian oil ash obtained as a result of combustion. The ash is considered as one of the key factors in selecting the proper utilization technology for Jordanian oil shale. For example, ash is known to affect the mode of combustion by affecting the heat flux and the deposition ash on the surfaces of the heat exchanger tubes in pulverized fuel combustors and fluidized bed combustors. The operational problems of slagging and ash deposition play a significant role in the design and the operation of a power generation facility. The present work is a part of an ongoing project to study the chemistry and the structure of ash produced from the combustion of Jordanian oil shale.

2. Experimental

2.1. Materials

A standard sample of oil shale was brought from the El-lujjun deposit, which is considered the largest deposit in Jordan, by the Jordanian Natural Resources Authority. Samples were crushed and sieved to less than 200 μm . Table 1 presents the proximate analysis for this oil shale.

Laboratory ashes from this oil shale were prepared by initially crushing the oil shale to < 150 μm , and ashing in an electrically-heated muffle furnace in accordance with the Australian Standards for ashing hard coal [9]. Fig. 1 represents a schematic diagram for the muffle furnace used in the experiment. One gram of oil shale is placed inside a silica crucible (diameter is 5 cm) and heated in air to 500 °C in 30 min. The sample is then heated from 500 to 815 °C in 60 min, and kept at 815 °C for 3 h to insure a constant remaining mass and hence complete combustion.

Table 1
Proximate analysis (air dry) for the oil shale used in this study

Property	Proportions (wt%)
Moisture	1.1
Volatile matter	44.0
Ash	54.5
Fixed carbon	0.4

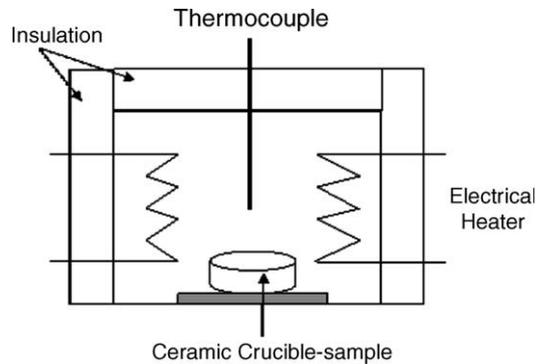


Fig. 1. Schematic diagram for the electrically heated muffle furnace used for the combustion process.

2.2. Samples analyses

1. *Particle size distribution.* Particle size distributions for the oil shale and oil shale ash were measured using the Malvern Master Sizer Model 2605, a laser diffraction particle sizer. Samples are dispersed in iso-propanol to avoid dissolving any water-soluble phase present.
2. *X-ray Fluorescence (XRF).* X-Ray Fluorescence Spectrometry (XRF) is an analytical technique used to identify or measure the concentration of elements present in solid, powdered or liquid materials. XRF for the samples utilized a Philips PW1404 Wavelength Dispersive Sequential XRF Spectrometer controlled by Philip X40 software.
3. *X-ray diffraction (XRD).* X-ray diffraction involves the determination of the structure of crystalline solids by an analysis of the diffraction patterns produced when X-rays are passed through the sample.

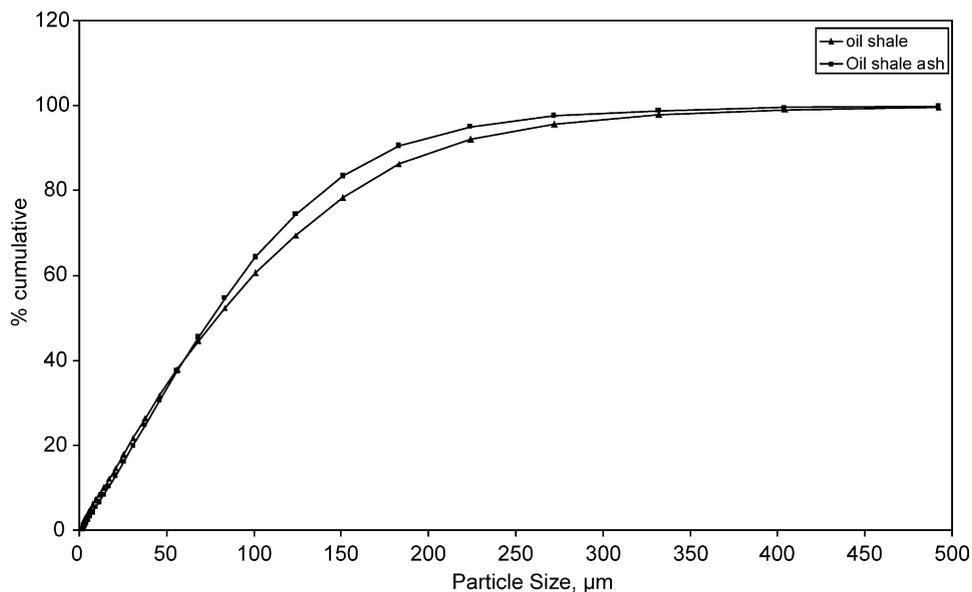
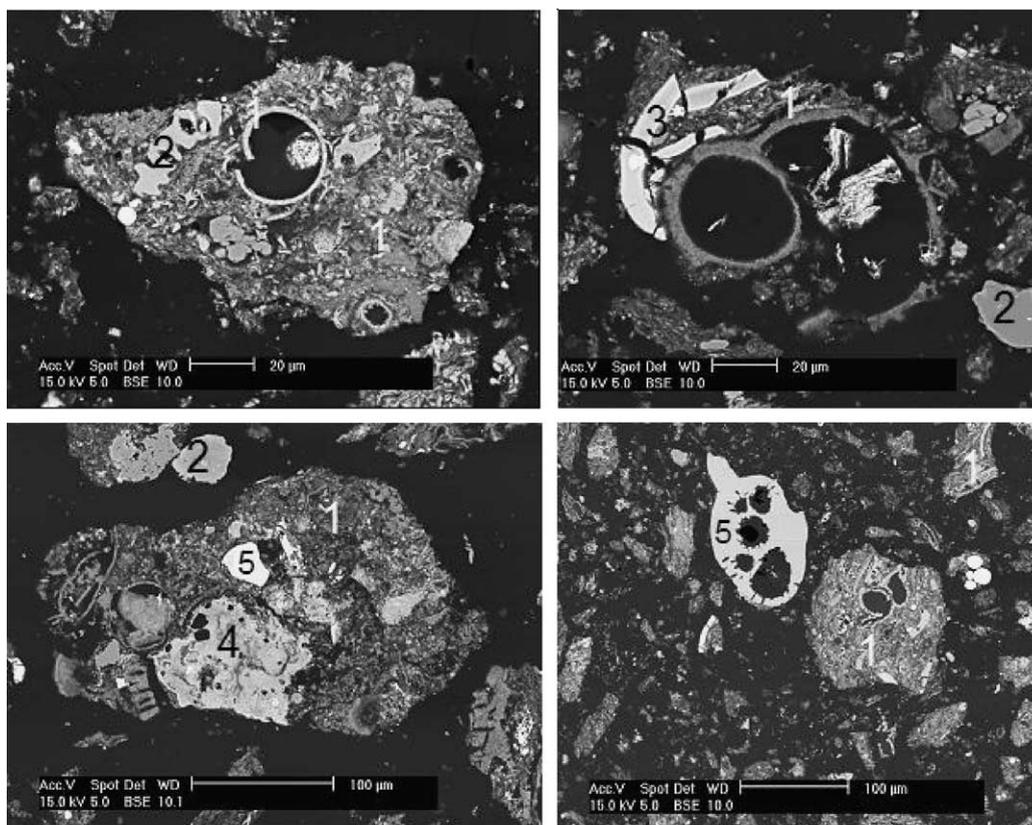


Fig. 2. The particle size distribution for oil shale and oil shale ash resulted from combustion.

Samples may be in a solid or powdered form, with an advantage of this technique since it is non-destructive. For this study, samples were analysed in powdered form using a Philips model diffractometer. Samples were analysed using a stepping scan from 3 to 90° two-theta. The step size is 0.02° two-theta, with a counting time per step of 1 s.

4. *Scanning electron microscope (SEM)*. SEM is a qualitative or semi quantitative technique useful for obtaining particle composition and morphology. A JEOL JSM-840 SEM with an attached Oxford Isis Energy Dispersive System (EDS) is used in this study. The typical operating parameters for the instrument are: a beam current equal to 3 nA, and an acceleration voltage of 15 kV. The working distance varied from 15 to 39 mm. Beside the chemical analysis, SEM is used to obtain images for the distribution of minerals in oil shale.
5. *QEMSCAN analysis*. The QEMSCAN system was developed by CSIRO/Australia. QEMSCAN is a relatively new automated system that rapidly determines mineral distributions in ores and processing-plant products. Originally designed for mining and mineral applications, QEMSCAN has also found broad application in the exploration, coal and oil and gas industries [10].



1. Calcite 2. Clay 3. Silica 4. Calcium Phosphate 5. Iron oxide

Fig. 3. SEM for oil shale showing different phases of minerals.

3. Results and discussions

From the particle size analysis for both the oil shale and the oil shale ash as seen in Fig. 2, it is clear that the particle size for both are very similar. This suggests that there is very small number of fragmentations occurred during combustion or ashing in laboratory furnace. This was expected since the Jordanian oil shale contains large proportions of ash (as will be described below). These high proportions are expected to maintain the original structure of the oil shale particle. This means that the amount of kerogen in the Jordanian oil shale is relatively low. Fragmentation is normally expected to occur due to the internal pressure build-up inside solid fuel particles during devolatilization of the oil or kerogen. However, the stagnant conditions of the experimental combustion process may have helped the particles of oil shale to maintain its original size. This result may provide essential information for the modelling of combustion.

The analysis from the energy dispersive spectrum (EDS) in the scanning electron microscope shows that the major phases in oil shale are present as calcite, clay, and quartz. It was surprising to see the oil or kerogen in the oil shale was encapsulated inside a shell of minerals, mainly calcite. The analysis of this kerogen using EDS showed that it mainly consists of carbon, hydrogen and sulphur. Fig. 3 shows samples of some SEM images for cross-sections of oil shale particles. These images show the minerals and spherical shells which encapsulate the kerogen. A thorough analysis by the EDS–SEM indicated that there was very little inorganic sulphur, which is mainly bounded to iron atoms forming pyrites. Sulphur was mainly present in the organic part of oil shale (in the kerogen). The XRD for oil shale supported the findings from the EDS–SEM. It is clear from Fig. 4 that calcite is the dominant phase in the minerals of the oil shale. Clays and quartz in addition to the phosphate were also present in different proportions.

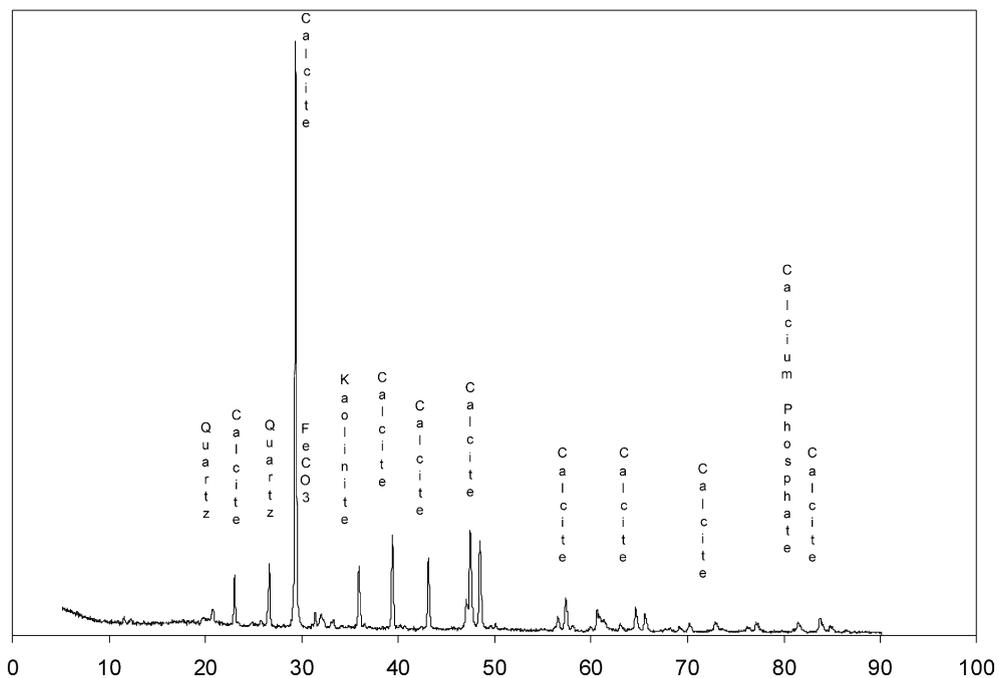


Fig. 4. XRD for the Elujjun oil shale.

The Qemscan was also employed to analyse and visualise the distribution of minerals in oil shale. The dominant phase recognised by the Qemscan was also the calcite, which is also represented by the calcareous matrix in Fig. 5. It is important here to mention that Qemscan detected a considerable amount of pyrite. This was expected since the size of the analysis beam in the Qemscan is 2 μm . Detecting any of the sulphur in the organic part along with iron in the surrounding shell could result in the anticipation of the formation of pyrite. It is worth mentioning that there was no uniform distribution of any of the detected minerals inside any oil shale particle. However, it was clear that there were some pure particles of calcite in the results of Qemscan. This information could help in the physical separation of kerogen rich minerals from pure minerals like floatation.

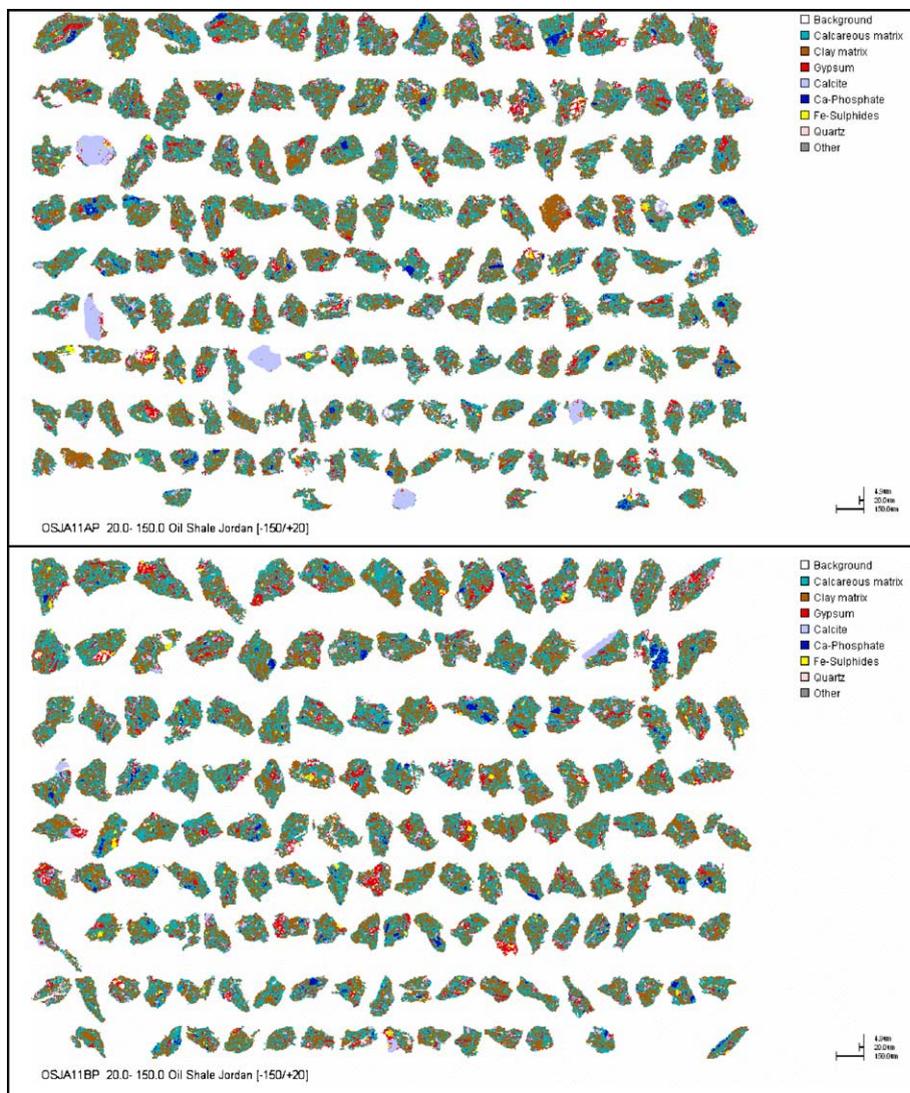
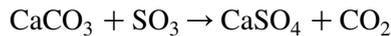


Fig. 5. Qemscan analyses for two samples of oil shale.

Table 2
The analysis of the El-lujjun oil shale ash as determined by XRF

Component	Proportions (wt%)
SiO ₂	26.6
Al ₂ O ₃	7.2
Fe ₂ O ₃	2.9
CaO	43.4
MgO	0.8
Na ₂ O	0.3
SO ₃	9.1
P ₂ O ₅	5.9

Results from XRF (Table 2) and XRD (Fig. 6) for the oil shale ash showed that, after combustion, some of the calcite is converted into anhydrite because of the sulphation reaction;



This transformation is explained by a simple suggested mechanism shown in Fig. 7. Oxygen diffuses through the shell of the calcite to perform the oxidation process of the fuel, which contains the sulphur. As a result, sulphur dioxide (SO₂) is produced and further oxidized to sulphur trioxide (SO₃). SO₃ then reacts with the calcite to produce the anhydrite (CaSO₄). Even though oil shale contains relatively large quantities of sulphur, the amount of sulphur released to the atmosphere is expected to be small since there are enough quantities of calcite to capture most of the sulphur.

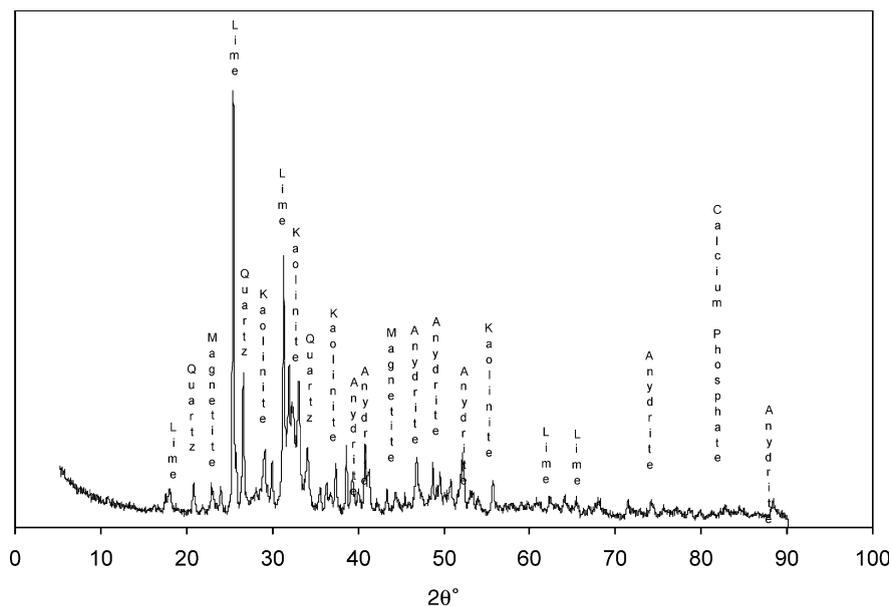


Fig. 6. XRD for the Elujjun oil shale ash.

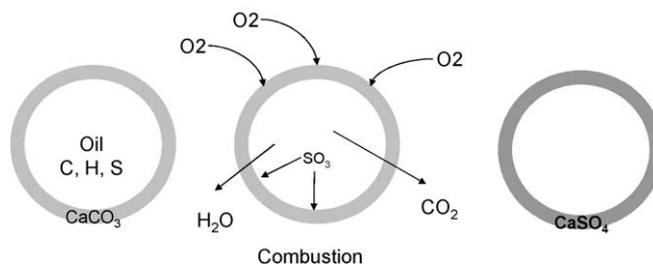


Fig. 7. Proposed mechanism for the formation of anhydrite.

4. Conclusions

During combustion, fragmentation of oil shale particles is minimal. The particle size distributions for both oil shale and oil shale ash are almost identical.

Different analytical techniques were used in this study to understand the transformation of minerals during combustion of oil shale. The dominant phase found in the oil shale was the calcite. Different proportions of clays, quartz, and phosphate were also present. There was no consistent distribution of minerals in oil shale particles. However, some pure calcite particles were also found in the sample of oil shale.

Sulphur was found to be mainly in the organic part of the oil shale. The organic part was found to be encapsulated by a shell of mineral, mainly calcite. Some inorganic sulphur was detected only by the Qemscan. During combustion, it is expected that the oxidation product of organic sulphur react with the calcite, which acts as a sulphur sorbent media, to produce the anhydrite.

Acknowledgements

The authors wish to thank Dr Alan Butcher from CSIRO/Australia and Dr Raj Gupta from the university of Newcastle/Australia for their help in the Qemscan analysis.

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