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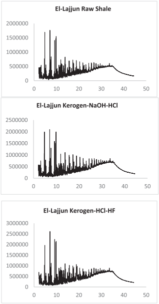
Full Length Article

A comparison of the NaOH-HCl and HCl-HF methods of extracting kerogen from two different marine oil shales

Jameel S. Aljariri Alhesan[a], Mohammad W. Amer[b], Marc Marshall[a], W. Roy Jackson[a], Thomas Gengenbach[c], Ying Qi[a], Martin L. Gorbaty[d], Peter J. Cassidy[e], Alan L. Chaffee[a,*]

[a] School of Chemistry, 17 Rainforest Walk, Monash University, Victoria 3800, Australia
[b] Department of Chemistry, Faculty of Science, The University of Jordan, Amman, Jordan
[c] CSIRO Materials Science and Engineering, Bayview Avenue, Clayton, Victoria 3168, Australia
[d] Fuels Science Consulting, 6635 Via Dante, Lake Worth, FL 33467, USA
[e] The Sentient Group, Suite 1, Level 17, 1 Castlereigh St, Sydney, NSW 2000, Australia

GRAPHICAL ABSTRACT



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ABSTRACT

The organic matter (kerogen, defined as including the organic material soluble and insoluble in organic solvents at room temperature) from two marine oil shales, El-Lajjun (Jordan) and Julia Creek (Queensland, Australia), has been extracted by the commonly used HCl-HF method and the resulting products compared with those obtained using the NaOH-HCl method, i.e. with initial strong alkali extraction. The elemental analyses on a dry ash-free basis of the solids obtained by the two methods were similar to each other and to that of the original oil shale. The pyrolysis-gas chromatography–total ion chromatograms were also similar for the kerogens obtained by the two methods and for the original oil shale, showing regular *n*-alkene/alkane series, as would be expected from the high atomic H/C ratio, and series of alkyl substituted thiophenes and benzothiophenes. The solid state ^{13}C NMR spectra showed similar trends. The Fe contents of the solids obtained by the HCl-HF treatment were much higher than for the solids from NaOH-HCl treatment, which could have implications for reactivity studies. XPS showed depletion of the sulfur and oxidation near the surface and confirmed that some aliphatic sulfur was present. However, in general, both methods gave organic products with similar characteristics, allowing isolation of organic matter by a method not involving HF, whose use is restricted in many countries.

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* Corresponding author.
E-mail address: alan.chaffee@monash.edu (A.L. Chaffee).

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1. Introduction

There is much interest in the structure of the organic component of oil shales, often referred to as kerogen [1–3]. The major fraction of this material, usually greater that 80% of the organic matter (OM) [4], is not soluble in common organic solvents under mild conditions. However, in view of the ambiguity of the word kerogen (which can refer to total OM or bitumen-free OM), other expressions have been used below to identify the products of chemical treatment of the oil shale.

In an earlier study it was shown that the humin (alkali and acid insoluble) isolated by NaOH-HCl treatment following a method originally suggested by McCollum and Wolf [5] was similar in elemental analysis and pyrolysis-gas chromatography–mass spectrometry (Py-GC–MS) to the OM of the original oil shale for two marine shales [6]. However, the most common method of isolating OM from oil shale is the use of HCl-HF [1,7–10]. It would therefore be of interest to determine whether the organic material isolated by the two methods was similar in its analytical properties, because, if so, the NaOH-HCl method could be used instead of the HCl-HF method, which is restricted in many countries because of safety concerns. Furthermore, if the chemical similarity of the humin fraction of the OM extracted by the NaOH-HCl method to the OM extracted by the HCl-HF method could be established, this would have interesting implications as to the structure of the oil shale organic matter. Therefore, in this paper, the characteristics of OM separated by the two methods are compared, utilizing solid state ^{13}C NMR and XPS in addition to elemental analysis and Py-GC–MS used in the study of OM isolated by the NaOH-HCl method [6].

2. Experimental

2.1. Materials

Oil shale from the El-Lajjun deposit from the Karak region in Jordan was supplied by Jordan Energy and Mining and oil shale from the Julia Creek deposit, Queensland, Australia was provided by Extract Oil (Global Oil Shale). These samples were ground to pass through a 180 μm sieve. Before analysis, oil shale samples were dried in a 105 °C oven under N_2 to constant weight. X-ray diffraction (XRD) for EL-Lajjun oil shale indicated that the minerals present were calcite ($CaCO_3$), making up over 40 wt% dry basis (db) of the oil shale, quartz and, in small amounts, kaolinite and apatite [4]. HCl-soluble iron, probably in the form of oxide, was also present [4]. The main minerals in Julia Creek oil shale were calcite, making up more than 20 wt% db of the shale, and quartz. Other silicates present were mainly mica, muscovite and clinochlore [11]. There was also more than 4 wt% db of pyrite [11].

NaOH solutions were prepared from high purity sodium hydroxide pellets supplied by Merck and HCl solutions were prepared from analytical grade 32% hydrochloric acid stock solution provided by Ajax Finechem Pty Ltd. Acid treatment with 48% hydrofluoric acid (HF) provided by Central Drug House (CDH) was done at the Department of Chemistry, The University of Jordan, Amman, Jordan. Deionized water was used in all treatments and washing steps.

2.2. Oil shale demineralization

2.2.1. NaOH/HCl demineralization procedure

The procedure used was that suggested by McCollum and Wolff [5]. In a typical procedure, 100 g of ground oil shale sample was mixed thoroughly with 310 g (50%w/w) NaOH solution in a 2 L stainless steel beaker. The beaker was covered, heated up to 160 °C in a N_2 purged oven and kept in the oven for 8–16 h at 160 °C. The beaker was agitated for a few minutes many times in the oven to ensure mixing of oil shale with NaOH solution. After cooling, the solidified base-treated oil shale was divided into smaller pieces, less than 16 mesh, reslurried with water, sieved to pass through a 16 mesh screen, washed with 5–10 L of water with decantation and filtered at room temperature. The decantation and filtration removed unreacted NaOH. The NaOH treatment converted the silica and silicates to hydrated alkali silicates, which remained insoluble in water [12]. In other experiments, the base-treated El-Lajjun oil shale was first filtered without water washing and this filtrate immediately acidified using dilute HCl. The resulting precipitate, so-called humic acid (alkali-soluble but acid-insoluble), was collected, dried and ashed as described in Section 2.3. The water washing of the NaOH-treated oil shale was then continued as before. After filtration, the solid was stirred with 2 M HCl for 1 h at room temperature and then filtered by vacuum filtration. The acid dissolved the hydrated alkali silicates and also the water insoluble carbonates [12] .Finally the solid was washed with water several times until the pH of the filtrate was 5–6, then dried at 70 °C under N_2.

2.2.2. HCl/HF/H_3BO_3 demineralization procedure

The procedure used was chosen to be the one most commonly used so that the results would be of general significance [10]. In HCl/HF/H_3BO_3 treatment, the raw oil shale was stirred for 24 h with 10% HCl solution at room temperature, filtered in order to remove the carbonates, which are soluble in HCl, and then the sample was dried in a 105 °C oven. After this, the carbonate free oil shale was mixed with 48% HF solution and stirred for 24 h at room temperature. The solution was carefully filtered and washed with water to remove the excess HF. The sample was mixed with 1:1 HF/HCl solution, stirred for 24 h at room temperature and filtered. The HF treatments converted the silica and silicates to fluorides, which would be either volatile or retained in the mixture. The reason that HF is effective and other halogen acids are not is that the Si-F bond is much stronger than the Si-O bond so that e.g. SiF_4 is thermodynamically more stable than SiO_2, whereas the other silicon halides are not [13]. The resulting solid product was stirred with a saturated solution of boric acid for 6 h at room temperature in order to bring into soluble form fluorides such as CaF_2 formed in the HF treatment [9,14]. The mixture was filtered to remove these salts. Finally, the solid was stirred with concentrated HCl for several hours at room temperature, filtered to remove any salts remaining from previous treatments and washed with water until the filtrate was free from chloride as shown by addition of $AgNO_3$ solution. The resulting solid was dried at 70 °C and kept in a sealed container. Some of the limitations of the procedure used will be mentioned below.

2.3. Oil shale and demineralized product characterization

Both types of treatments were repeated until low ash yields were obtained so that OM can be studied with minimum effects caused by the presence of the mineral part. The ashing was carried out at low temperature (490 °C) for 5–7 h in order to minimize the reactions between carbonate and silicate minerals [4] so that the ash content would be similar to the mineral content. The heating was repeated for several periods until the rate of weight loss became constant.

Elemental analysis for C, H, N, S, Cl for original oil shale and demineralized product (DP) samples and determination of Fe content for DP ashes were carried out at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. The O analysis was calculated by difference and the values of organic C, H, N, S and O on a dry mineral matter free (dmmf) basis were calculated from the elemental analysis and ash content of the DPs.

Py-GC–MS analysis was carried out on a Chemical Data Systems (CDS) Pyroprobe 5200 connected to a GC–MS (Agilent 6850 GC and 5790 MSD). An accurately weighed sample of 0.20–0.25 mg was placed in a quartz tube with a quartz wool plug at each end and the tube inserted into the platinum heating coil of the Pyroprobe. The coil was heated under helium initially to 100 °C for 1 s, rapidly ramped to 650 °C at 10 °C/msec and kept at 650 °C for 15 sec. The products of the thermal treatment were then released through a heated transfer line (320 °C) under a helium flow to the GC–MS. The boiling point distribution of the pyrolysates was characterized by classifying the chromatogram peaks