DISSOCIATION OF ORGANIC AND MINERAL MATRIX OF MAOMING OIL SHALE AT LOW-TEMPERATURE AND AMBIENT-ATMOSPHERE

ARTHUR SHU-KEUN LEE, HSIEN JEN LIAN, TEH FU YEN*
(University of Southern California)
Los Angles, California, USA

ABSTRACT

On the basis of the analytical results, the Maoming oil shale sample contains approximately 25.5% kerogen, 1.25% bitumen, 1.2% moisture, and 63.3% ash. Among the mineral content, a semi-quantitative analysis of FT-IR spectroscopic technique indicated that this oil shale is dominant in kaolinite associated with montmorillonite interstratified with illite and amesite as accessories.

In an alkaline aqueous environment, the presence of sodium ions can swell the structural layers of clays. The hydroxyl ions can decompose the silicate and alumino-silicate structures, providing that ultrasonic radiation and electrolytic current are applied simultaneously. This results in dissociation of clay minerals and organic complexes. An enrichment of organic matter up to 44.3% can be derived in residual shale from the dissociation process.

The dissociation phenomena of organic complexes and mineral matrix are significant. Very likely, it will lead to a new technology for processing organic matter as well as mineral aggregates.

1. INTRODUCTION

The total resource of oil shale in China is estimated to be as much as two thousand billion tons which is equivalent to eighty billion tons of shale oil [1]. The major mining sites are in Fushun and Maoming. In the early 1960's, Maoming began operation at the rate of five million tons per year. The high content of organic matter (20 to 26% by weight) makes Maoming oil shale an important oil shale resource in China.

*Current address: 213A BHE, University of Southern California, L. A., CA 90089-0231, U.S.A.

Oil shale consists of two major organic fractions, soluble bitumen and insoluble kerogen, which are potentially good raw materials for plastic and synthetic fiber industries. The kerogen fraction appears to be more than the bitumen fraction, and it is tightly bonded to the mineral sediment, making the recovery process difficult. The most popular recovery method used today is the retorting process which is essentially a pyrolysis reaction.

Current retorting method is very inefficient with respect to liberating the organic material found in oil shale. At best it can remove 70% of the organic material contained in shale rock. The remaining 30% is connected to the inorganic matrix and is not available as an energy source. For every barrel of oil produced, the retorting phase alone would require net energy roughly equivalent to 3/25 of a barrel of shale oil. The result of gas formation during the pyrolysis reaction appears to be a net loss of organic materials. This is particularly true for coal-like types of oil shale.

In spite of the disadvantages mentioned above serious environmental problems, such as wastewater treatment and deposition, air pollution, groundwater contamination, etc., have no immediate solution yet. Therefore, the authors have attempted to search for a new method of recovering organic matter from oil shale at low-temperatures and ambient-atmospheres. The idea is based on the swelling properties of clays in alkaline aqueous solutions containing swelling agents (e.g., ethanol). When the solution is subjected to ultrasonic energy and electrolytic current, the hydroxyl ions can decompose the silicate and aluminosilicate structures. As a result, organic and mineral matrix are dissociated and suspended in the solution. This paper discusses the experimental results of the dissociation phenomena for the Maoming oil shale.

2. EXPERIMENTAL

Experimental procedures have been described in a previous paper for application to an Australian shale [2]. Only one step has been added to the previous procedure. There was a 0.3 ml. of hydrogen peroxide added to the anode chamber four times in every 2-hour interval.

3. RESULTS AND DISCUSSION

A. Organic and Mineral Characteristics of Maoming Oil Shale

On the basis of the analytical results, the Maoming oil shale sample contains approximately 26.8 % (by weight) organic matter, 1.2% moisture, and 63.3% ash. This gives an estimate of combined water to be 8.7%. An FT-IR (Fourier Transform Infrared) spectrum of raw shale is shown in Figure 1A.

The soluble organic matter (bitumen) is about 1.25% of the total oil shale as determined by the Soxhlet extraction method. The insoluble organic portion (kerogen) obtained from the acid digestion of the mineral phase is approximately 25.5%. Their FT-IR spectra are shown in Figure 1C and 1B respectively.

FT-IR spectrum of the kerogen in KBr (Figure 2B) shows absorption of paraffinic structure at 2920, 2850, 1454, 1370 cm^{-1} with a small peak at 720 cm^{-1} which may be an indication of straight chains having more than four CH_2 groups. The absorption band at 1710 cm^{-1} is due to C=O stretching of carbonyl and carboxyl. It is fairly broad and does not show details. Therefore we are not able to differentiate between various components. At a high degree of evolution, it may be reduced to a weak shoulder. Another fairly broad absorption band is centered at 1623 cm^{-1}. The existence of these two absorption bands may indicate that the kerogen comes from a shallow deposit. FT-IR spectrum of bitumen in CCl_4 is also shown in Figure 2C. Both of them do not show any absorption at 1575 cm^{-1} for the presence of salts of carboxylic acids.

The X-ray diffraction spectrum of the Maoming oil shale shows that the minerals present are mostly clays. Clay minerals are dominant in kaolinite associated with montmorillonite interstratified with illite, amesite and other minerals including quartz, siderite, pyrite and strontianite.

The FT-IR spectrum of the raw oil shale in KBr confirms those minerals found by the X-ray diffraction technique. Figure 2A shows the raw shale IR spectrum, and Figure 2B shows a mineral spectrum derived after a subtraction of kerogen IR spectrum from the raw shale IR

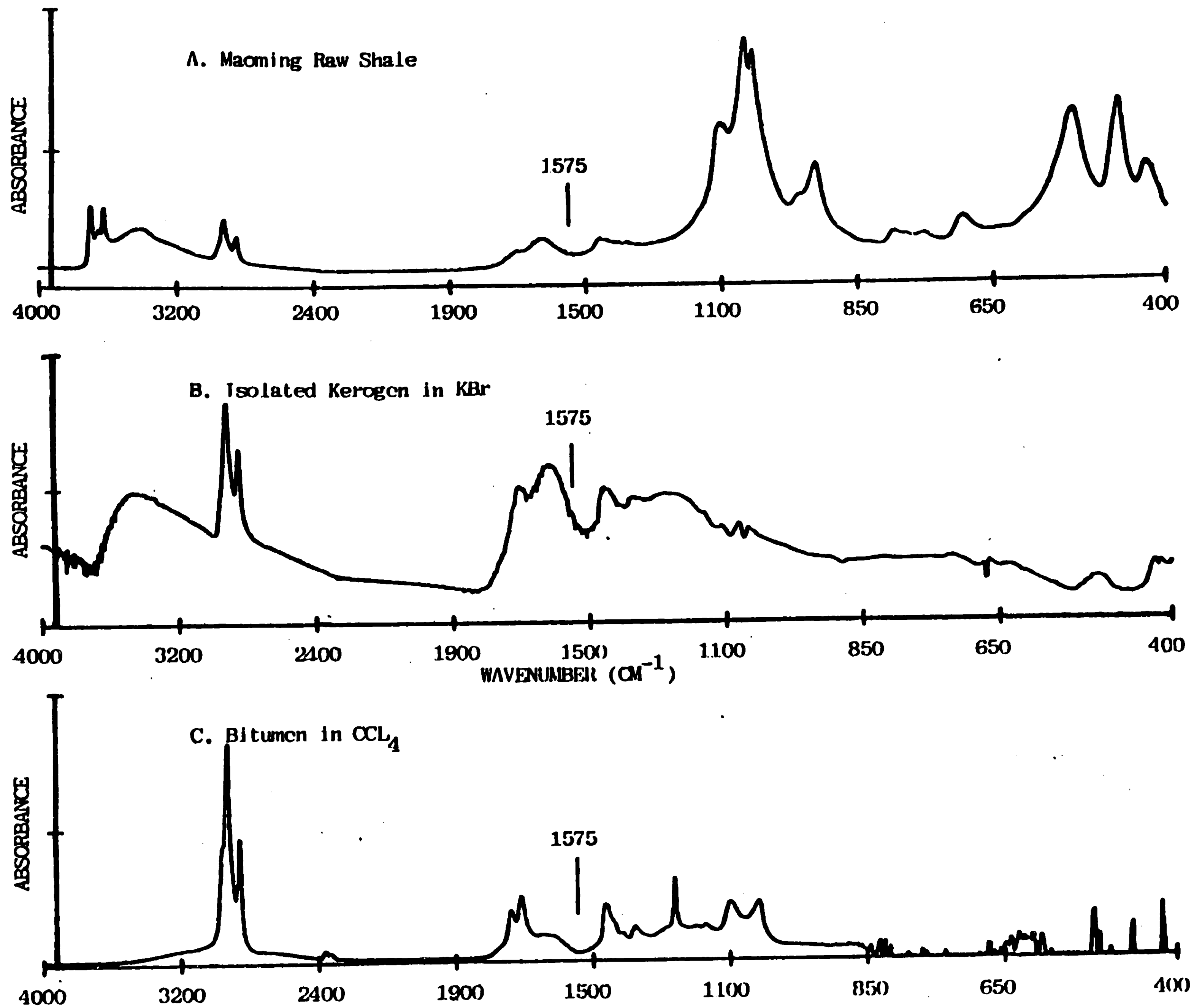

Figure 1. FT-IR Spectra of (A) Maoming Raw Oil Shale, (B) Isolated Kerogen in KBr, and (C) Bitumen in CCl_4.

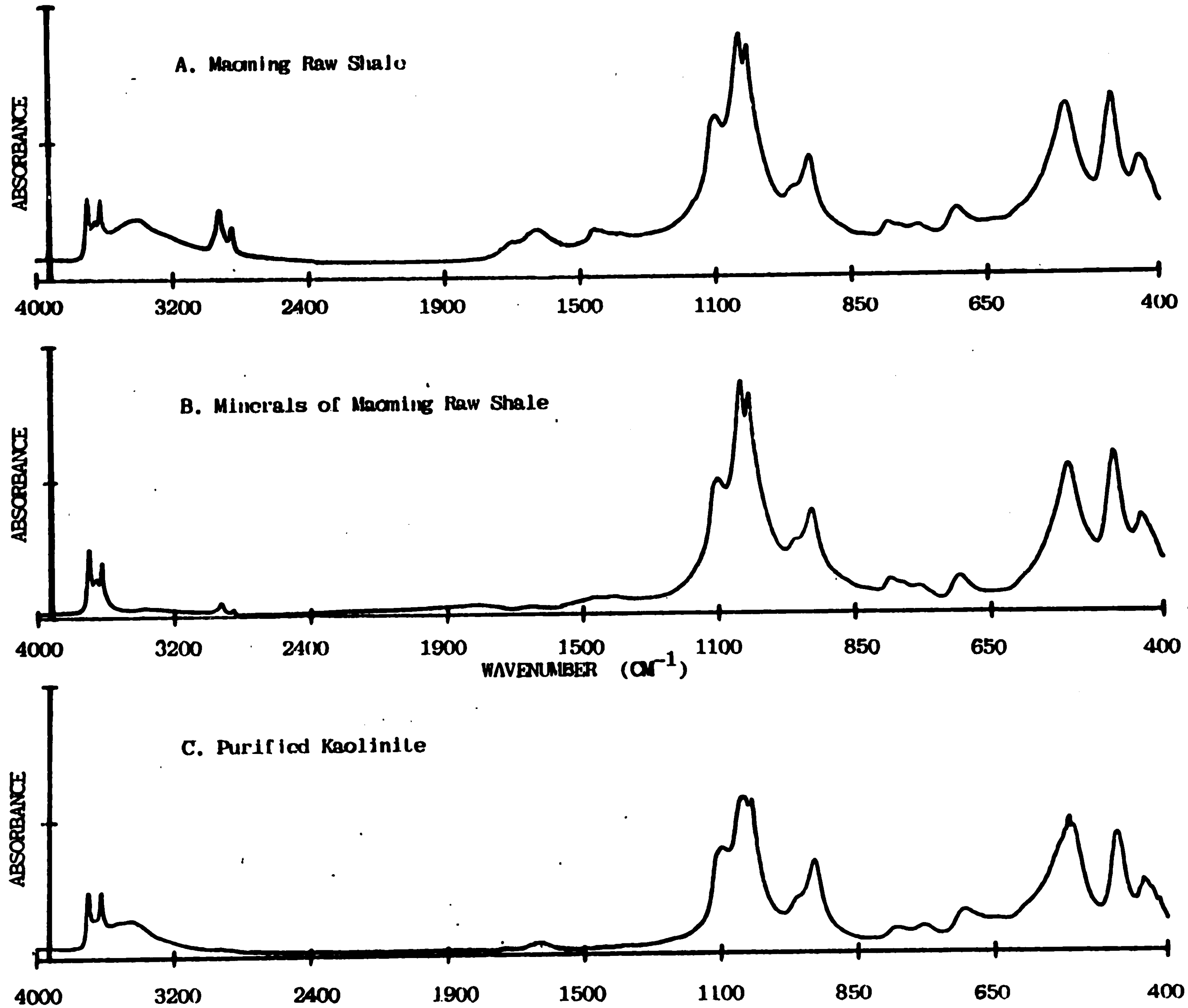

Figure 2. FT-IR Spectra of (A) Maoming Raw Oil Shale, (B) Minerals of Maoming Raw Oil Shale, and (C) Purified Kaolinite Standard.

spectrum has been done. The major peaks of this mineral spectrum match perfectly with the kaolinite IR spectrum shown in Figure 2C. By performing a series of subtraction from the known and quantified mineral IR spectra, the quantity of each mineral would be obtained. The results indicated that Maoming oil shale is dominant in kaolinite associated with montmorillonite interstratified with illite and amesite as accessories. Other minerals including quartz, siderite, pyrite and strontianite are present in trace amounts (less than 5%).

B. Dissociation of Maoming Oil Shale

A series of swelling tests were conducted to test the nature of Maoming oil shale. It was found that the presence of 30% by mole of ethanol in an aqueous solution after 4 hours of sonication could swell 1 gram of oil shale into a full volume of 10 ml of solution. Hence, a swelling treatment was carried out prior to the dissociation experiment. 3.0 grams of raw shale was swelled in a 10 ml ethanol aqueous solution after one hour of sonication. Then this 10 ml solution was placed in the anode chamber with a total of 500 ml of 3N sodium hydroxide solution.

After ten hours of dissociation process, only 78% by weight residual shale was left in the anode chamber. An FT-IR spectrum of this residue in Figure 3B showed that major minerals are dominant in illite and montmorillonite, and kaolinite is reduced to an accessory level with 12.5% sodium salts (e.g. sodium carbonate). The organic matter was estimated to be 44.3% by the quantitative comparison in the FT-IR spectrum and was confirmed with the ash technique.

The FT-IR spectrum of this organic matter shows a dramatic change in the absorption band around 1575 cm^{-1} which is neither presence in the original kerogen nor in the bitumen. The absorption of this peak is believed to be due to the presence of carboxylates. This is an indication that the kerogen is destroyed by the electrolytic oxidation (with a small additive of hydrogen peroxide) in conjunction with ultrasonication. The reaction may proceed through membrane-mimetic mechanisms.

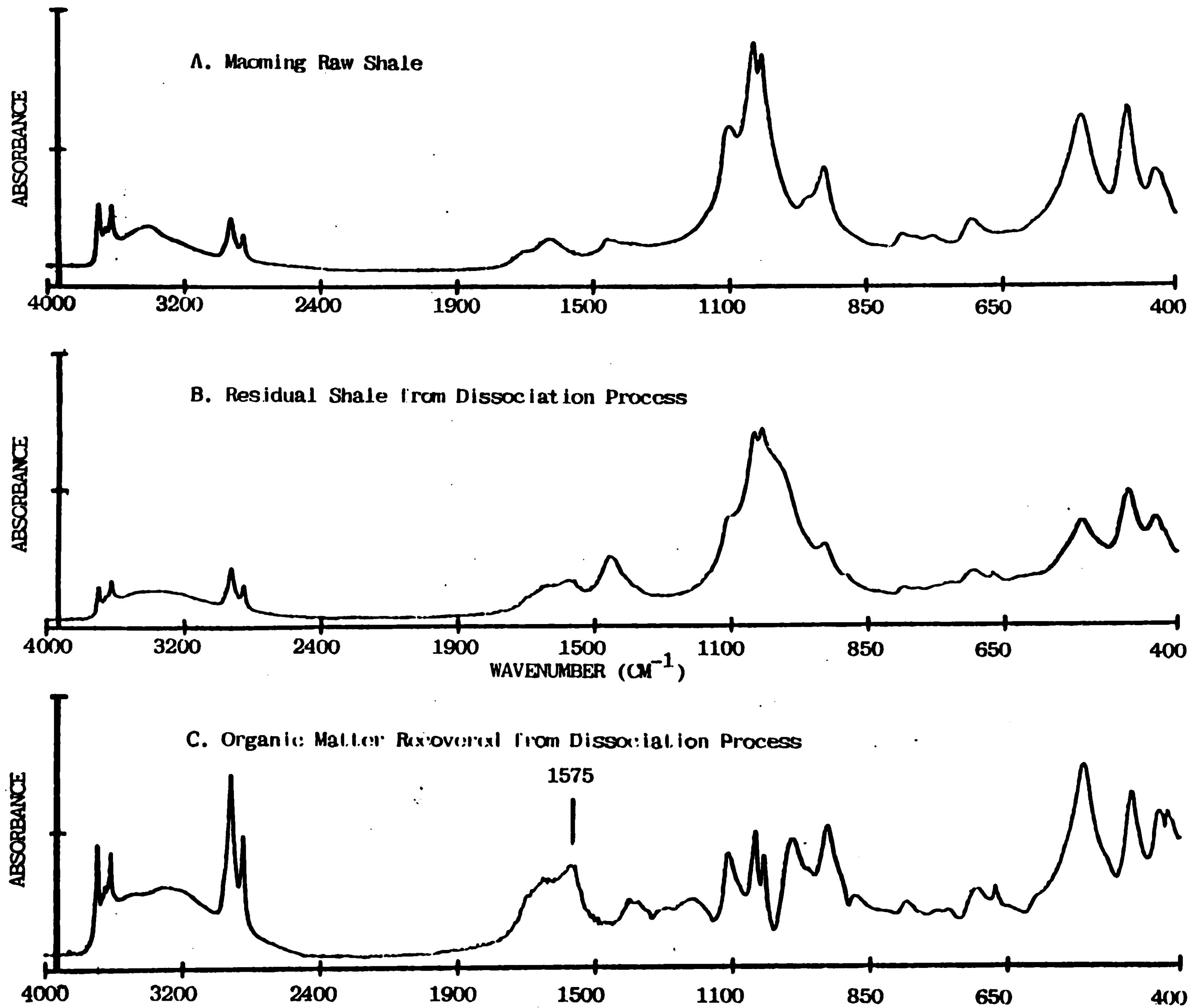

Figure 3. FT-IR Spectra of (A) Macming Raw Oil Shale, (B) Residual Shale from Dissociation Process, (C) Organic Matter Recovered from Dissociation Process.

In microscopic study of the solution obtained from the dissociation process, many ordered forms of liquid crystals were found, and they all showed positive optical activity under polarizing light. These liquid crystals suggested that surfactants were arranged themselves in an ordered form of vesicles. The surfactants could be very likely derived from the destruction of kerogen during the dissociation process.

4. CONCLUSION

The dissociation phenomena of organic complexes and mineral matrix are significant. Physical evidence shows that major portions of the kaolinite and some other clay mineral are dissociated from the mineral matrix. These result in the liberation of organic matter from the shale matrix as well as in the opening of channels for other active species, such as ions, radicals, and other organic reagents that react with the newly explored surfaces, thus increasing the dissociation of organic matter. Also, electrolytic oxidation is shown to be important in oxidizing part of the kerogen complexes as shown by the abundance of carbonyl and carboxylic matter in the process solution.

Furthermore, such destruction of kerogen may lead to a new technology for the processing of organic matters as well as the mineral aggregates. However, more studies are needed to better understand this phenomena and the operating variables.

5. REFERENCES

[1] Hou, X. L. (Editor), "Shale Oil Industries in China," Petroleum Industrial Publishing House, 1984.

[2] Lee, A. S., Sadeghi, M.-A., and Yen, T. F., "Characterization of Stuart Oil Shale System: I. New Method of Releasing Organic Matter," accepted and to be published in Energy & Fuels, 1988.