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THERMOGRAVIMETRY AND COOL PLASMA ASHING OF TIMAHDIT OIL SHALE

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ABSTRACT

The decomposition of Timahdit oil shale has been studied by thermogravimetry and by cool plasma ashing. The effect of particle size and heating rate of reaction has been investigated. Products of decomposition have been examined by scanning electron microscopy.

INTRODUCTION

Retorting conditions such as heating rate, nature and flow rate of gas used, particle size of material, are important factors which govern the oil yield during the processing of oil shales. Campbell et al (ref. 1) studied the effect of heating rate on oil evolution during pyrolysis of Colorado oil shale blocks and powder. They found that at lower heating rates, the reaction rates are greater but the oil yields are lower. These authors investigated also the effect of inert gas (argon) flow rate on oil yield. Wallman et al (ref. 2) investigated the effect of particle size on oil yield. Rajeshwar (ref. 3) studied the kinetics of kerogen decomposition during pyrolysis by thermogravimetry. His work confirms the effect of heating rate on kinetics of the reaction, and he determined two values for the activation energy at low and high heating rates. These were attributed to the decomposition of kerogen to bitumen and decomposition of bitumen to gas, oil and carbonaceous residue. Kinetic studies relating to determination of activation energy and order of reaction have been carried out by Arnold et al also (refs. 4, 5). The work of Campbell et al (ref. 6) and of Noble et al (refs. 7, 8) give comparable results for activation energies determined by isothermal and non-isothermal methods.

Recently we have studied the change in sample dimension and organic matter distribution in relation to shale bedding during pyrolysis of Timahdit

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oil shale (refs. 9, 10). These results show that the material exhibits anisotropy with respect to distribution of organic matter as well as to dimension changes during reaction.

In this work we report the effect of particle size and heating rate of Timahdit oil shale.

EXPERIMENTAL

Sample Preparation

The oil shale used in this work was obtained from the layer M of Timahdit (Morocco). The samples were crushed for 20 minutes and sieved for 30 minutes to obtain different particle size fractions.

Thermal Analysis

Thermal analysis were carried out on a Stanton-Redcroft STA 781 thermal analyser using samples of 10 mg in flowing nitrogen atmospheres (35.5 cm^3 min^{-1}).

Carbon burn-off was carried out at low temperatures also using an Anton Paar cool plasma asher in oxygen - argon atmospheres (approx 2% Ar) at 27 MHz frequency.

Residues after burn-off were studied by TG.

Scanning Electron Microscopy

Selected samples of the oil shale and of its reaction products were examined using JEOL model JSM-35C scanning electron microscope. The samples were coated with a uniform layer of gold using an Edwards Sputtercoater S150B to ensure electrical conductivity (deposition rate 15 nm min^{-1}).

RESULTS AND DISCUSSION

Figure 1 shows the percentage weight loss for three different particle size fractions of Timahdit oil shale at a heating rate of 10 ^{o}C min^{-1}. Three different steps are observed on the weight loss curves. A loss of about 1.3% between ambient temperatures and 150 ^{o}C is attributed to evolution of moisture. Between 200 ^{o}C and 520 ^{o}C a second weight loss of 12.5 - 14.0% occurs due to decomposition of organic matter. From 520 to 800 ^{o}C the weight losses are the result of decomposition of mineral matter, mainly calcite and dolomite. The results show that particle size has no effect on the curves during loss of moisture and organic matter. However, the third weight loss due to mineral matter decomposition is greater for the smaller particle size fractions.

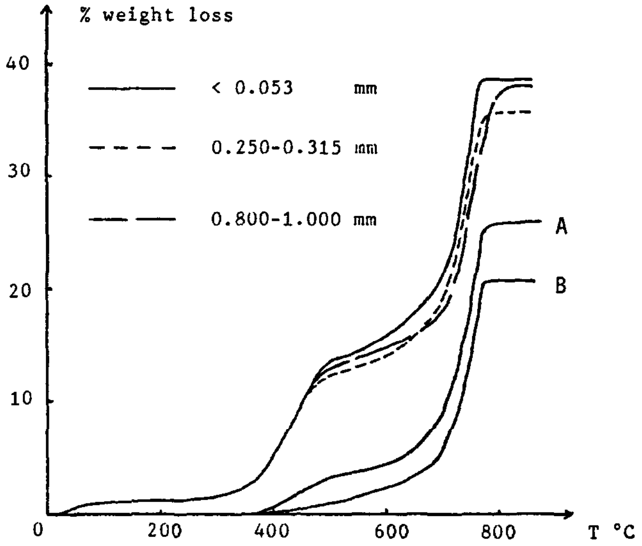

Figure 1: TG Data showing weight loss of oil shale samples for three different particle size fractions of original material and products of plasma ashing for two size fractions (A: 0.250-0.315 mm, B: < 0.053 mm)

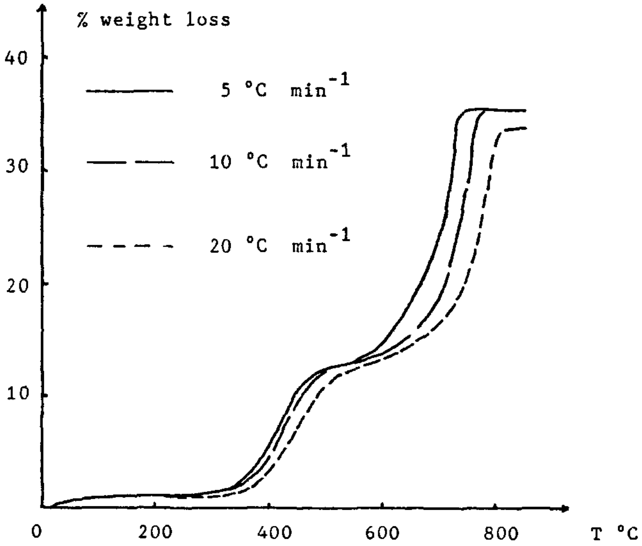

Figure 2: TG Data showing effect of heating rate on oil shale pyrolysis for the 0.250 - 0.315 mm particle size range.

Figure 2 shows the effect of heating rate on the weight loss for the material of particle size range 0.250 - 350 mm. The extent of decomposition at a given temperature increases for lower heating rates.

Carbon burn-off in the plasma asher is shown for two different particle size ranges in Figure 3. A higher rate of burn-off as well as a larger limiting weight loss is observed with the smaller particle size fraction. This is in contrast with TG results (Figure 1) where particle size had no effect on rate of decomposition of organic matter. In the plasma asher the reactivity towards oxygen is governed by the available surface, which is higher for a given weight of smaller particles, and by the rate of diffusion of gas through the particle.

Weight losses during TG of the final residues (after more than 8 hours ashing) are shown in Figure 1 under the same conditions as for the raw oil shales (10 $^{o}C\ min^{-1}$ heating rate and 35.5 $cm^{3}\ min^{-1}$ nitrogen flow rate). The results show that during cool plasma ashing all the moisture and most of the volatile organic matter are evolved.

Figure 4 shows the weight losses during 1 hour pyrolysis in flowing nitrogen (35.5 $cm^{3}\ min^{-1}$) of 0.200 - 0.250 mm particle size fraction samples (sample size 2 g) of Timahdit oil shale in a tube furnace at different temperatures. The cold samples were introduced to the furnace pre-set at a fixed temperature. The shape of the curve is similar to that of the TG curves of the new samples in Figure 1. The two steps in the weight loss curve are attributed as in TG to loss of organic matter and decomposition of mineral matter.

Scanning electron microscopy was used to investigate textural changes of the oil shale during the decomposition reactions. Figure 5(a) shows the 0.200 - 0.250 mm particle size fraction of unreacted Timahdit oil shale. Figures 5(b), 5(c) and 5(d) are the same material heated for 1 hour in a tube furnace in flowing nitrogen at 317, 667 and 840 ^{o}C respectively. These correspond to weight losses of 5.9, 22.5 and 40% of original sample (see Figure 4).

At 317 C ^{o}(Figure 5(b)) small particles of product material are seen on the surface of the large particle. This is due to "pitting" caused by evolution of volatile matter from the material, and this continues at higher temperatures as seen in Figure 5(c) for the product obtained at 667^{o}C. At

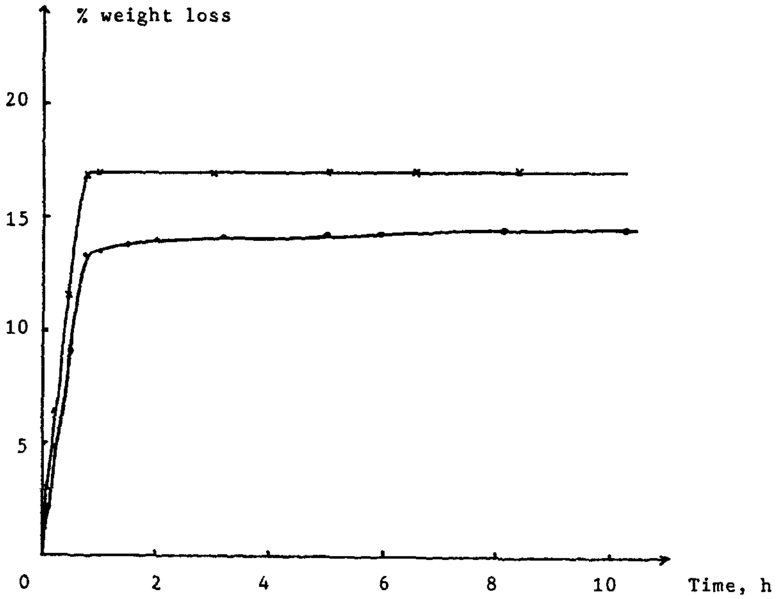

Figure 3: Effect of particle size on oil shale decomposition during plasma ashing; x : 0.053 mm and • : 0.250 - 0.315 mm

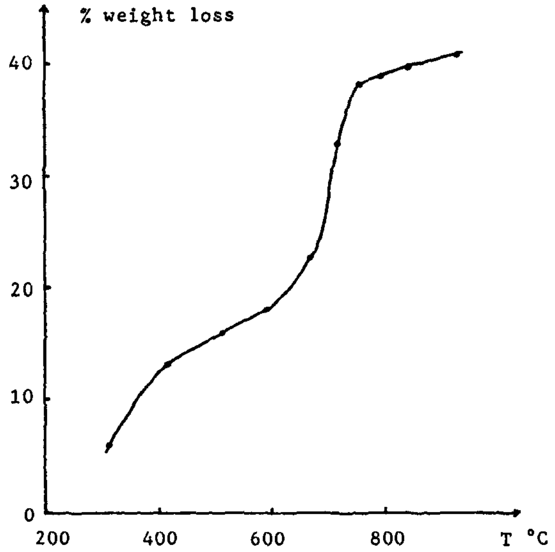

Figure 4: Percentage of weight loss during one hour pyrolysis in flowing nitrogen.

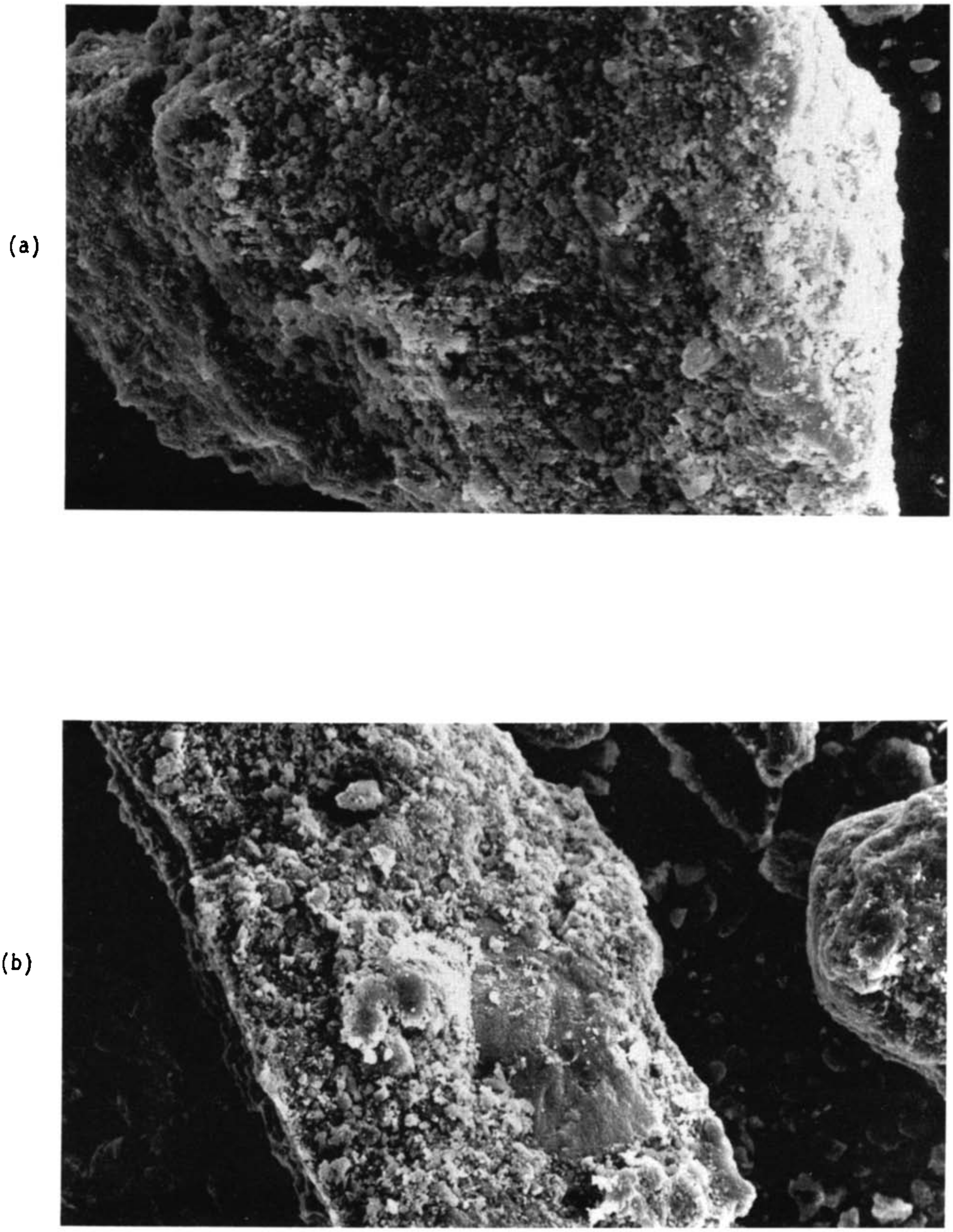

Figure 5 : SEM of (a) unreacted oil shale (magnification 430) and (b) sample decomposed at 317 °C. Particle size: 0.200 - 0.250 mm (magnification 430).

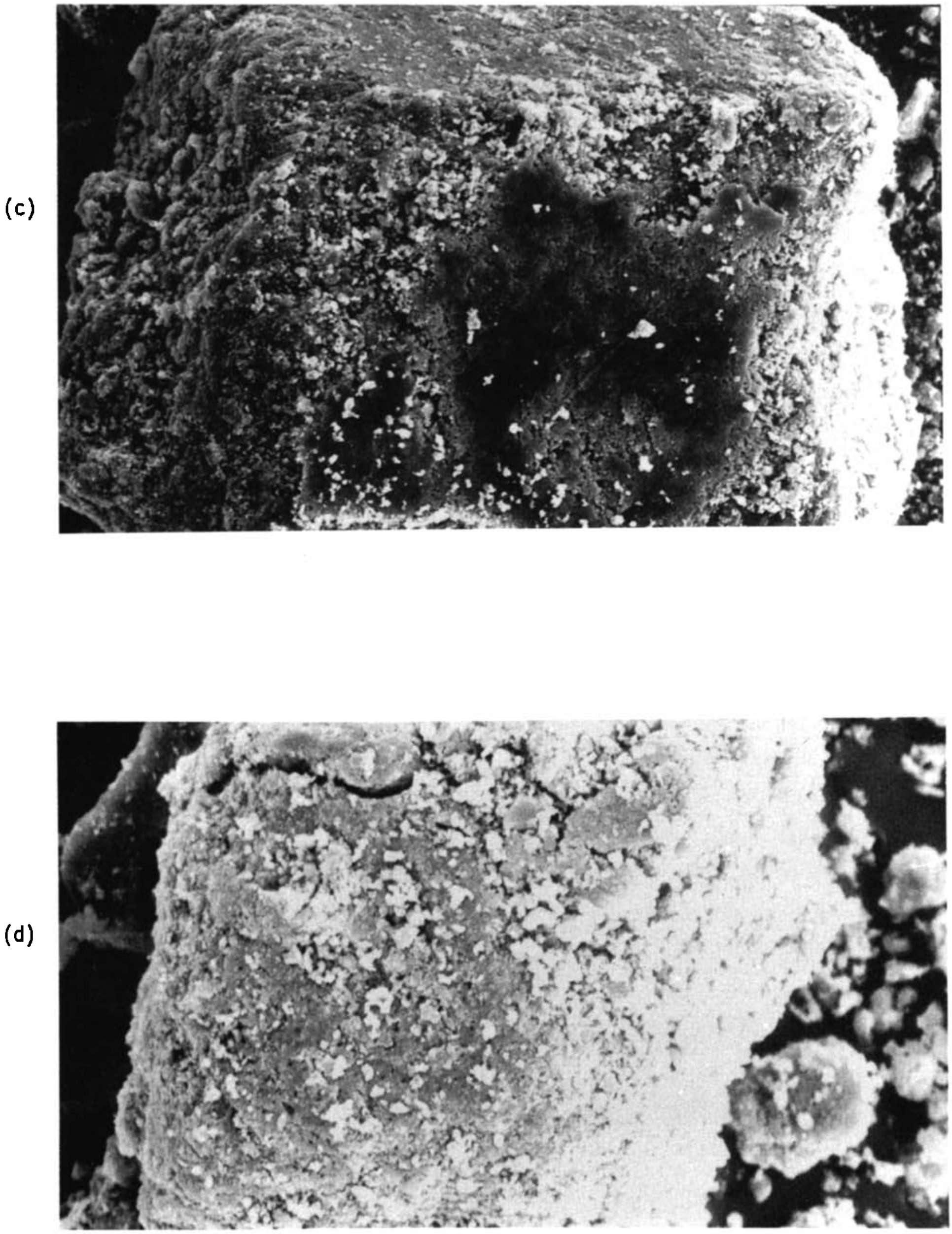

Figure 5 : SEM of (c) sample retorted at 667 °C (magnification 390) and (d) retorted at 840 °C. Particle size: 0.200 - 0.250 mm (magnification 650).

temperatures approaching 700°C, large cracks are visible and more globules appear on the surface of the particle (see Figure 5(d) for sample heated at 840°C). These cracks are probably due to the mineral decomposition which occur in the temperature range considered (see Figures 1 and 4).

Figure 6(a) shows the 0.053 mm particle size fraction of the original oil shale. Figures 6(b) and 6(c) are of this material after ashing for 15 minutes and 8.5 hours respectively. Significant changes in the appearance of the material occurred after 15 minutes. This corresponds to a weight loss of just over 6% (Figure 3), and the changes are similar to those observed after 6% weight loss at 317 °C in a nitrogen atmosphere (Figures 4 and 5(b)). After extensive periods of ashing, the volatile matter is mostly removed and the crystalline mineral matter is relatively unchanged (Figure 6(c)).

Scanning electron microscopy of the 0.250 - 0.315 mm particle size range after ashing do not show such good crystallinity as in the small size fraction ashed products (see Figure 6(d) which is the result of 30 minutes ashing of the 0.250 - 0.315 mm fraction). This is because removal of organic matter from larger particles is more difficult and causes more disruption to the surface.

CONCLUSION

In the pyrolysis of Timahdit oil shale, the rate of evolution of organic matter is independent of particle size of material, but the rate of decomposition of mineral matter at higher temperatures is greater for small particles. However, heating rate does affect both organic matter evolution and mineral decomposition. This is in agreement with the previous work (refs. 3 - 5).

During cool plasma ashing, particle size governs the rate of decomposition of organic matter.

Significant textural changes are observed by scanning electron microscopy of the decomposed products during pyrolysis and plasma ashing of the oil shale.

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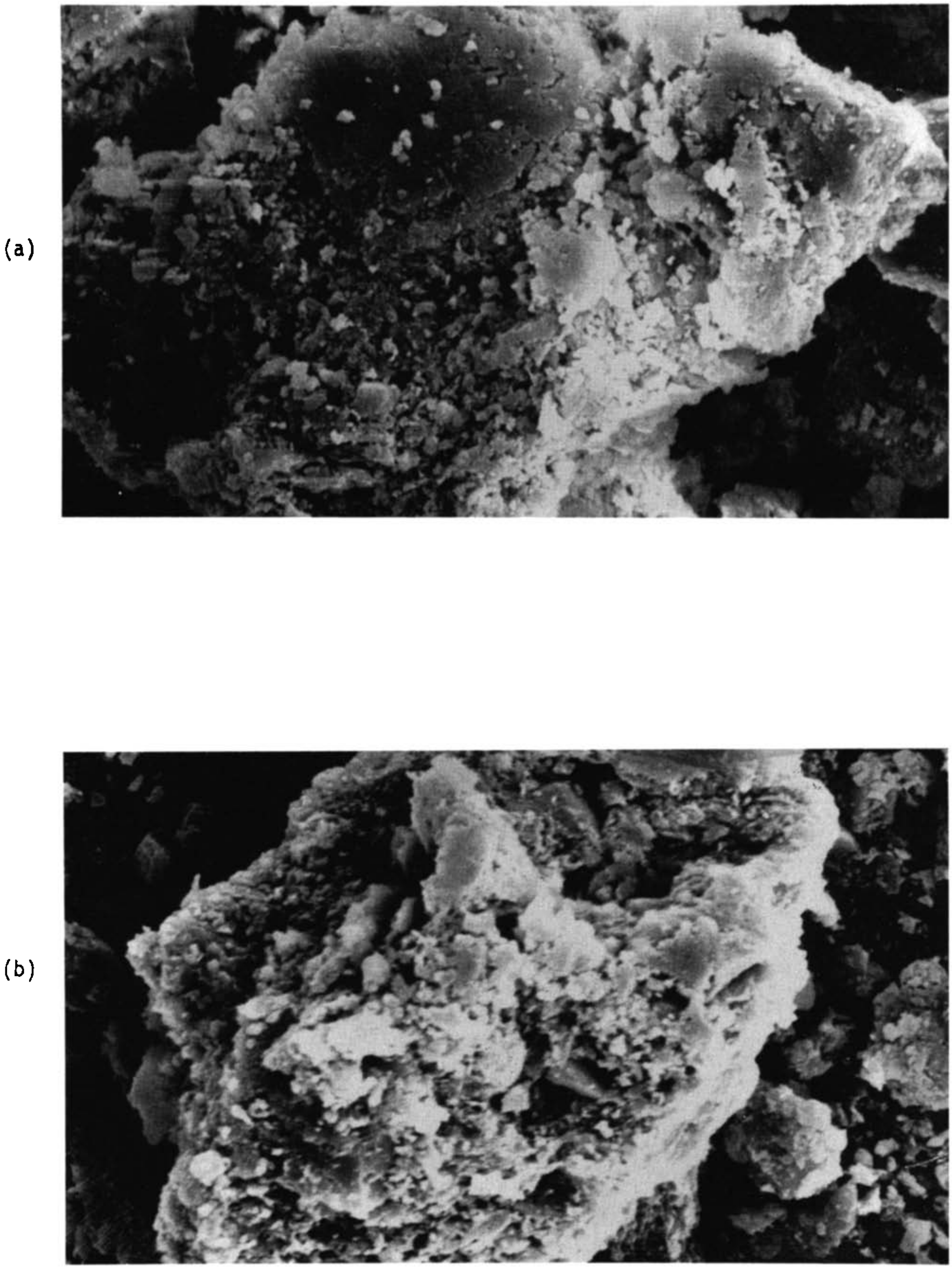

Figure 6 : SEM of (a) undecomposed sample (magnification 1200) and (b) sample decomposed in the Plasma Asher for 15 min. Particle size < 53 µm (magnification 1300).

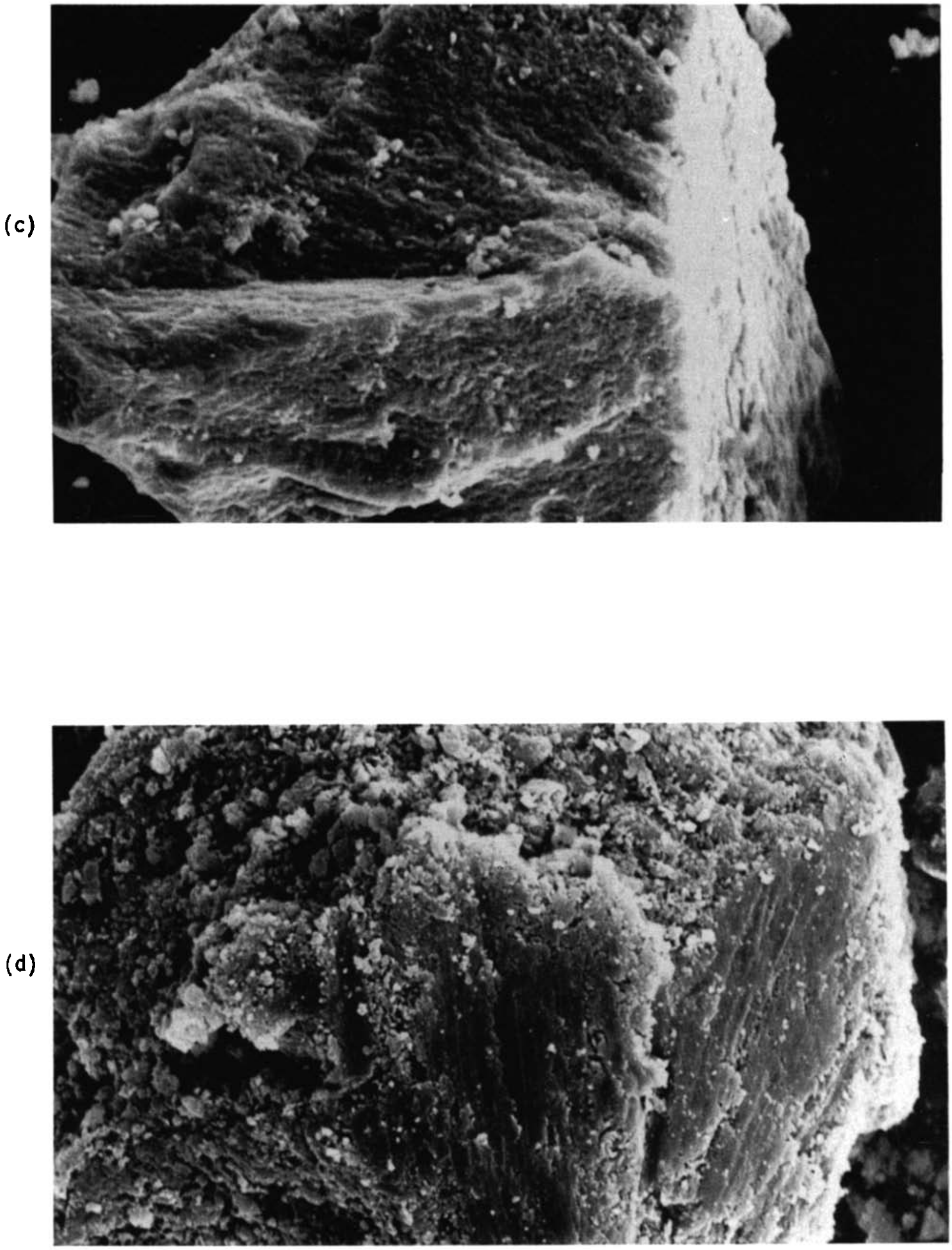

Figure 6 : SEM of samples decomposed in the Plasma Asher. (c) Particle size < 53 µm and time 8 h 22 min (magnification 1600). (d) 0.250 - 0.315 mm and 30 min (magnification 1000).

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