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INVESTIGATION OF THE ANISOTROPY OF TIMAHDIT OIL SHALE (MOROCCO) BY DILATOMETRY

H BARKIA [1], L BELKBIR[1], N GERARD [2] and S A A JAYAWEERA [3]

[1]Laboratory of Reactivity of Solid/Gas Systems, Department of Chemistry, Faculty of Science, Rabat, MOROCCO

[2]Laboratory of Research for the Reactivity of Solids, Faculty of Science, Mirande, 21000 Dijon, FRANCE

[3]Department of Chemistry, Teesside Polytechnic, Middlesbrough TS1 3BA, UK

ABSTRACT

The pyrolysis of Timahdit oil shale has been studied by thermogravimetry and by dilatometry. The material undergoes contraction depending on the direction of measurement relative to that of the shale bedding. The contraction is greater in the direction perpendicular to the shale bedding compared with the direction parallel to it.

INTRODUCTION

Thermal decomposition of oil shale has been the subject of numerous studies. The mechanism of oil shale decomposition is complicated due to several factors such as the location of the oil shale deposit, the non-uniform composition and distribution of the organic and inorganic material of the shale, the difficulty of separating large proportion of the organic material without chemically altering the material (ref. 1). These problems led workers to carry out their experiments on raw rock by using single particles of geometrical form of sphere, cylinder and cube (refs. 2-8). Thus, Allred (ref. 2) by using cylindrical samples of diameter range from 9.2 to 50.8 mm showed that the time required to remove 95% of the volatile matter from the cylinders varied approximately as the square of the particle diameter. A mathematical model of the pyrolysis of an oil shale particle, represented as an equivalent sphere, has been developed by Johnson et al (ref. 3) incorporating heat transfer and kinetics. In order to obtain a complete set of weight loss data on machined single particles of oil shale and to develop a corresponding mathematical description of the pyrolysis process, Granoff et al (ref. 4) showed that the samples developed numerous cracks and the relative size of the core diminished with increasing time and temperature.

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Barker (ref. 9) studied the variations of volatile bitumens and kerogen both along and across shale bedding. He concluded that the distribution of volatile bitumens is not controlled by the distribution of kerogen but shows evidence of bitumen movement through the clast. The amount and composition of the volatile bitumens and their distribution suggest that in part, they have been introduced into the clast from the surrounding medium, and that the movement of hydrocarbons occurs preferentially along the shale bedding plans (ref. 9).

Our recent studies of concentration profile of organic matter along and across the shale bedding plans showed that a gradient of organic matter is establsihed across shale bedding during pyrolysis of cubic samples at 345^{o}C for 5, 10 and 15 minutes (ref. 8). This is due to a diffusional phenomenon in Timahdit Moroccan oil shale. This paper reports the study of the role of sedimented planes on changes of sample dimension, and will provide information on behaviour of organic matter in oil shale during pyrolysis.

EXPERIMENTAL

The oil shale used in this work was obtained from the deposit of Timahdit (Layer M) (ref. 8). This stretches in a North-Easterly direction in Morocco. Its length is about 50 km and width 8 km. The prepared samples have a parallelepipedic shape and four faces perpendicular to the sedimented plane and two faces parallel to the same plane. These geometrical forms were obtained by polishing at room temperature and atmospheric pressure.

Weight loss data were obtained as described by Belkbir (ref. 10). A dilatometer study was carried out on a parallellepipedic form having a constant area of 25 mm^2 and a height ranging from 1.9 to 9 mm. These samples were introduced into a dilatometer under a nitrogen flow rate of 30 cm^3 min^{-1} and a heating rate of 58 ^{o}C min^{-1}..

The dilatometer functions (Fig. 1) as follows: the sample is held in position by a kanthal wire to the extremity of a thin quartz tube. The sample remains in this position due to a spring that links the other extremity of the tube to the kanthal wire. The movement of a master on the "free" extremity of the spring enables the change in dimension of the sample to be monitored.

Allowance for the expansion of the kanthal wire was made by carrying out measurements on two samples of different lengths. The difference in the measurements corresponds to the absolute expansion of a sample of length equivalent to the difference in length of the two experimental samples.

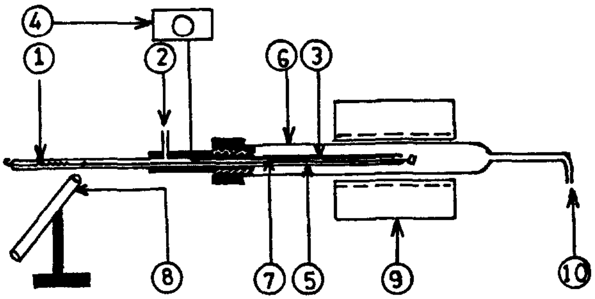

Figure 1: Schematic equipment of dilatometer. 1- Spring; 2- Gas in ; 3- Thermocouple ; 4- Galvanometer ; 5,6- Silica tube ; 7- Wire of Kanthal ; 8; Cathetometer; 9- Furnace and 10- Exhaust.

RESULTS AND DISCUSSION

Figure 2(a) shows the absolute variation (Δ L) of sample dimension (L) perpendicular to the shale bedding plane for samples of three different length. Figure 2(b) shows similar data parallel to shale bedding plane. Figure 3 shows this data for the dimension changes per unit length ($\Delta L/L$). The variation of sample dimension is greater in the perpendicular direction than in the parallel direction.

Figure 4 is the TG curve for the pyrolysis of the oil shale, showing three distinct regions corresponding to (i) dehydration, (ii) decomposition of organic matter and (iii) decomposition of mineral matter.

Comparison of Figure 4 with Figures 2 and 3 show correlations between weight and dimension changes. Thus, (i) loss of moisture is not accompanied by dilatometric changes; however, (ii) and (iii) decompositions of organic and mineral matter are accompanied by shrinkage of sample in both directions.

According to Jourdain (ref. 11), if an alumino-silicate compound contains 85-93% silica and 5% alumina, the total expansion of the materials is 0.6%. Our results show a contraction in the material of several percent depending on the direction of the sample. The oil shale we studied contains 23.4% silica and 5.3% alumina and is thus not comparable with the material studied by Jourdain. Also, it is difficult to distinguish between dimensional changes due to decomposition of organic and mineral matter.

Figure 5 shows the first derivative, d($\Delta L/L$)dT, of the linear contraction with respect to temperature of the sample direction. The curves show maxima at 410^{o}C where evolution of organic matter is also at a maximum (Figure 4).

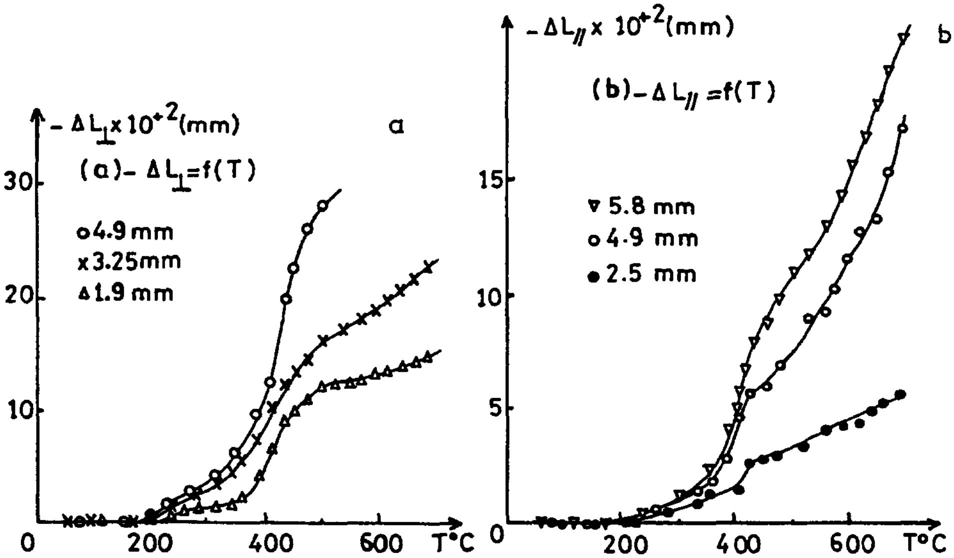

Figure 2 : Absolute variation of sample dimension versus temperature, heating rate 58°C/min ;(a) Perpendicular to shale bedding plane; (b) Parallel to shale bedding plane

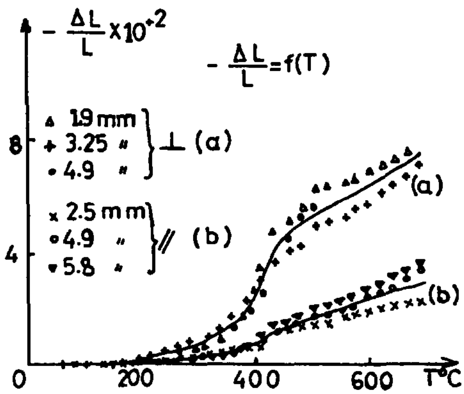

Figure 3 : Relative variation of sample dimension with temperature, (a) Perpendicular to shale bedding plane; (b) Parallel to shale bedding plane

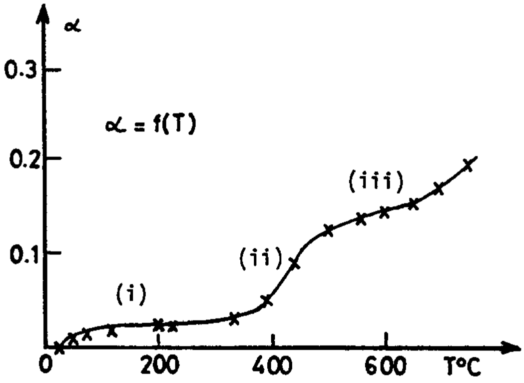

Figure 4 : Experimental conversion curve for the pyrolysis of Timahdit oil shale sample.

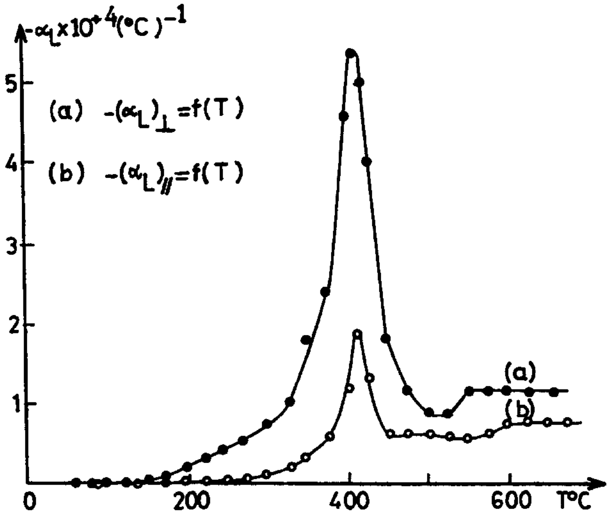

Figure 5 : Perpendicular (a) and Parallel (b) variation of linear contraction coefficient α_L with temperature.

CONCLUSION

The results show that the dimensional changes of oil shale are dependent on sample direction, the greater shrinkage occuring with sample perpendicular to the direction of shale bedding. Our previous work (ref. 8) on measurement of residual organic matter confirms the anisotropy of the material. Thus the structural anisotropy of the material is consistent with a compositional anisotropy.

REFERENCES

1 J F Mckay, Energy Sources, 7 (1984) 257
2 V D Allred, Quart. Colo. School Mines, 59 (1964) 47 [as cited in 4]
3 W F Johnson, D K Walton, H H Keller and E J Couch, Quart. Colo. School Mines, 70 (1975) 237
4 B Granoff and H E Nuttall, Jr., Fuel, 56 (1977) 234
5 T T Coburn and J H Campbell, "Oil Shale Retorting: II Variation in Product Oil Chemistry During Retorting of an Oil Shale Block", Lawrence Livermore Laboratory, Rept. UCRL-52256-2 (1977)
6 J H Campbell, G H Koskins, N D Stout and T T Coburn, In Situ, 2 (1978) 1
7 K Rajeshwar and J Dubow, Thermochim. Acta, 103 (1986) 147
8 L Belkbir, H Barkia and N Gérard, Thermochim. Acta, 103 (1986) 147
9 C Barker, Geochim. Cosmochim. Acta, 44 (1980) 1483
10 L Belkbir, Thermochim. Acta, 103 (1986) 13
11 A Jourdain, La Technologie des Produits Ceramiques refractaires, Ed.Gauthier-Villards (1969)