Thermochimica Acta, 152 (1989) 115-123
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THE KINETICS OF THE THERMAL DECOMPOSITION OF NATURAL MOROCCAN AND IRAQI PHOSPHATES.

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SUMMARY

Phosphate rock valorization aims by thermal treatment to eliminate humidity, organic matter and carbonate in order to increase the amount of P_2O_5.

This work consists in the study of both Moroccan and Iraqi phosphates by thermogravimetry, for differents particle size such as 0-200µm, 200-315µm, 315-500µm, 500-800µm, in argon , oxygen and air.

The thermal decomposition curves present between the ambient temperature and 1000°C show three domains of weight loss. These are assigned to dehydration (20-200°C), elimination of organic matter (200-550°C), and decomposition of carbonate (600-850°C) respectively.

The effect of particle size and the nature of transport gas on thermal decomposition have been investigated. On the other hand, sample phases have been studied by xrd before and after heating.

Activation energy(E) and frequency factor(k_0) attributed to phosphate decomposition have been determined by FREEMAN-CARROLL methods.

INTRODUCTION

Phosphate sedimentary ores with carbonate gangue have a large exploitable layer. Their valorization by thermal treatment allows by calcination in air the elimination of gangue. This type of treatment should in future take a large importance if the ores become poor.

The decomposition of carbonate is a very endothermic reaction[1] . So, the manufacturers have to master the thermal operations in order to improve the thermochemical yield.

Several authors [2,3] have investigated gangue elimination by chemical, mechanical and physical means.

For this study, we investigated by thermogravimetry the decomposition of carbonate in natural phosphate with a high amount of carbonate.

0040-6031/89/$03.50

EXPERIMENTAL

Naturalphosphate used in this work originated from Morocco and Iraq. Thermal decomposition of these mineralshas been carried out by TG for several particle size 0-200μm, 200-315μm, 315-500μm and 500-800μm and in different flow rate of argon,oxygen and air.

The thermobalance of type SETERAM,is characterized by a weight module situated below the sample,which is thermally isolated from the heat module. The latter consists of a resistance element in chromate of lanthanum which reach in oxidizing atmosphere a temperature close to 1600°C.

The measurement of temperatures is done with a monochromatic automatic pyrometer (λ= 0,65 μm). The aiming is done with a prism at total reflection. This pyrometric measurement is checked by thermocouple (Pt-Pt/Rh 30%) which is situated close to the sample.

Thermogravimetry is followed by X-ray diffraction which aim to monitor the materials' phases and to follow their behavior after different thermal treatment between the ambient temperature and 1000°C.

The apparatus used for powder analysis was a Philips diffractometer, copper K radiation was used.

Both compounds have the same structure as fluorapatite ($Ca_{10}(PO_4)_6F_2$) which crystallize in hexagonal system [3,4] .

Crystallinity of these compounds is clearly well defined in high temperatures[5].

RESULTS AND DISCUSSION

Preliminary studyallows to determine carbonate percentage in each particle size. This shows that 200-315μm is the less carbonated sample (5,5% for Morocco and 16% for Iraq). This result is independent of sweep gas nature used (fig.1). Thus kinetic studies were made on this particle size which is rich in phosphate.

NON ISOTHERMAL THERMOGRAVIMETRY

First approach of the phenomenon of sample thermal decomposition quoted previously has been made by TG.

- heating rate : 1.374°C/min
- sample weight : 10mg
- sweep gas atmosphere of argon, oxygen and air.

Thermogravimetric curves (fig.2) present between the ambient temperature and 1000°C show three successive domains of weight loss separated by two thermal stability zones.

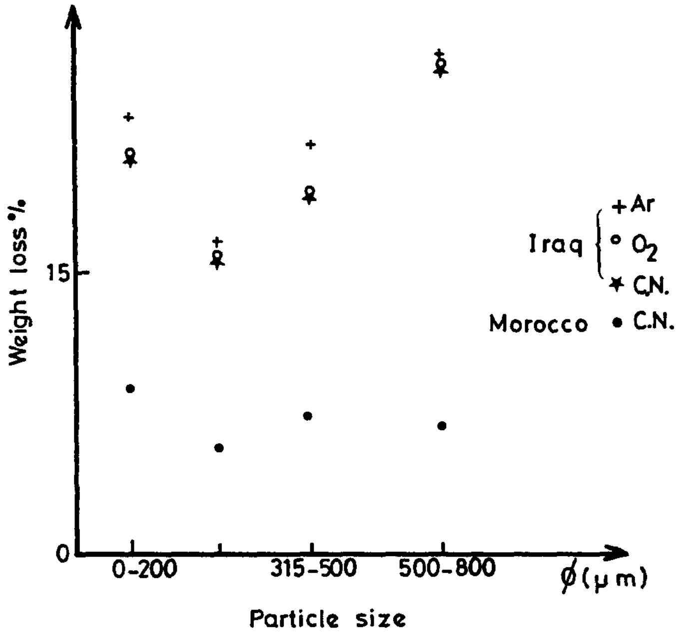


Fig.1: Weight loss variation versus particle size.

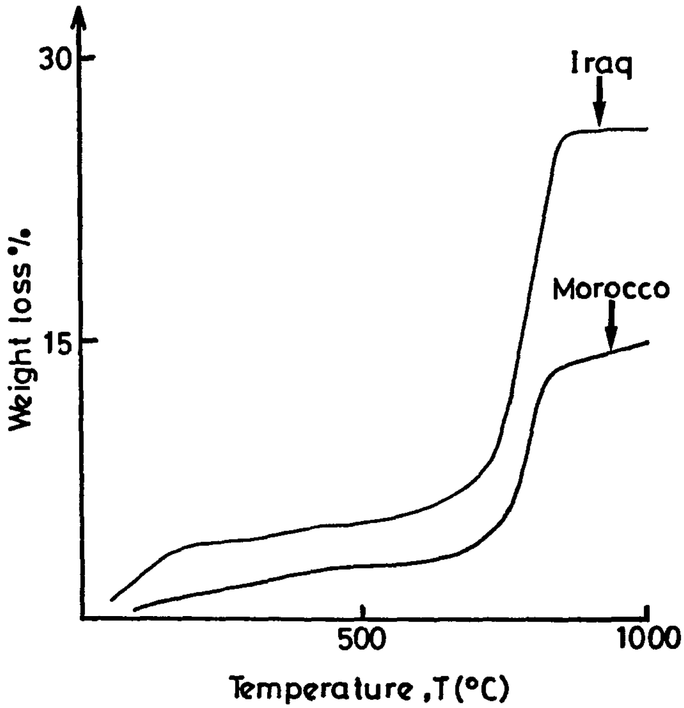


Fig.2: Thermogravimetric curve as a function of temperature for both samples.

The first weight loss presents rate maxima at 150°C for both minerals. This loss is attributed to the evaporation of free water in the sample[6]. Second loss occurs between 150 and 550°C and corresponds to organic matter elimination[3]. Concerning the third very important and complex weight loss, it mainly corresponds to decomposition of carbonate reaction[3]. The release of carbon dioxide is a continuous loss. This latter loss will be the subject of this work.

Samples studied were burnt at 500°C in order to eliminate water (1,5% for Morocco and 3,78% for Iraq) and all organic matter (0.5% for Morroco and 1,5% for Iraq) fig.3. [5].

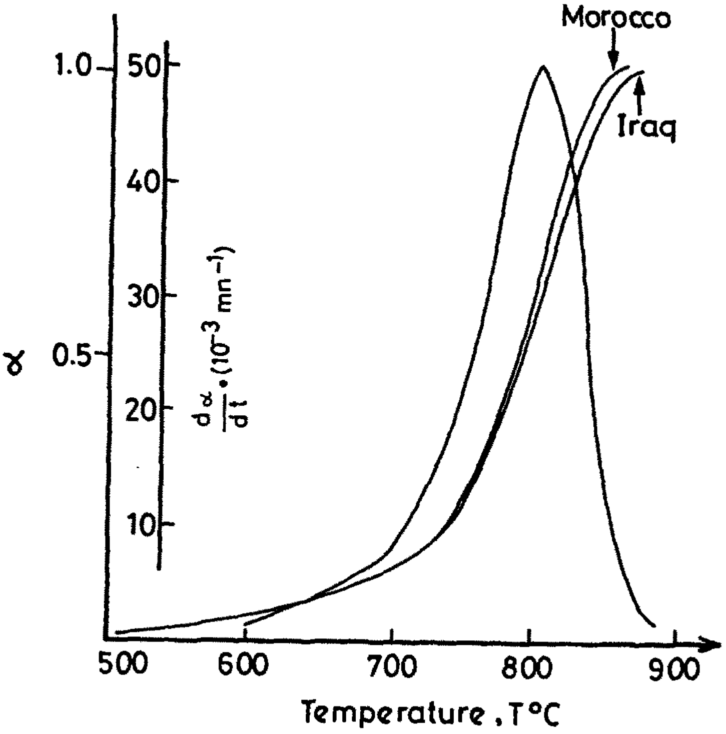


Fig.3: a)Fractional weight loss, α, as a function of temperature for sample.
b) Derivative thermogravimetric curve as a function of temperature for Iraqi sample.

The thermal decomposition of phosphate is of reaction type :

$$A_s \longrightarrow B_s + C_g \qquad (1)$$

Kinetics of solid state decomposition reaction may be represented by an expression of the form[7]

$$\frac{d\alpha}{dt} = k\ f(\alpha) \tag{2}$$

where α is the fraction reacted in the time t, k is the rate constant, and the function $f(\alpha)$ depends on the particular decomposition mechanism. The rate constant k is related to the absolute temperature T by the Arrhenius expression

$$k = k_0 \exp(- {}^{E}/_{RT}) \tag{3}$$

k_0 is the freqency factor, E is the activation energy and R is the gas constant. Substituting eqn.(3) in eqn(2), we get.

$$\frac{d\alpha}{dt} = k_0\ f(\alpha) \exp(- {}^{E}/_{RT}) \tag{4}$$

For a reaction which may be represented functionally as $f(\alpha) = (1-\alpha)^n$ where n is the reaction order, the above expression reduces to

$$\frac{d\alpha}{dt} = k_0 \exp (- {}^{E}/_{RT}) (1-\alpha)^n \tag{5}$$

The difference - differential method developed by Freeman and Carroll[8] offers the advantage of directly yielding the value of n.Again, starting with eqn.(6) and taking logarithms

$$\ln k_0 - \frac{E}{RT} = \ln (\frac{d\alpha}{dt}) - n \ln (1-\alpha) \tag{7}$$

Differentiating eqn.(7), we get

$$\frac{E}{R} d (- \frac{1}{T}) = d \ln (\frac{d\alpha}{dt}) - n\ d \ln (1 -\alpha) \tag{8}$$

Integration of the above equation yields

$$-\frac{E}{R} \Delta (\frac{1}{T}) = \Delta \ln (\frac{d\alpha}{dt}) - n \Delta \ln (1-\alpha) \tag{9}$$

Dividing eqn.(9) by $\Delta \ln (1-\alpha)$ we get

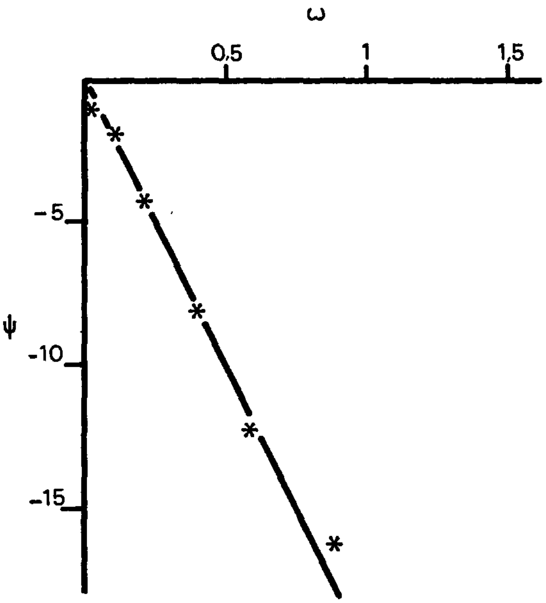
$$-\frac{E/R\,\Delta (1/T)}{\Delta \ln (1 -\alpha)} = \frac{\Delta \ln (d\alpha / dt)}{\Delta \ln (1-\alpha)} - n \tag{10}$$

A plot of $\Delta(1/T) / \Delta \ln (1-\alpha)$ vs. $[\Delta \ln (d\alpha /dt)] / [\Delta \ln (1-\alpha)]$ should yield a straight line according to eqn. (10) from which values of E and n may be determined from the slope and intercept.

Fig.3 illustrates the fractional weight loss, α, as a function of temperature or time for phosphates. The sigmoid-shaped conversion curves characterise solid-state decomposition reactions. The raw TG data were used to generate values at each temperature from the following equation.

$$\alpha = \frac{W_0 - W_t}{W_0 - W_f} \tag{11}$$

where W_0 = initial mass of sample, W_t = mass of sample at time t and W_f =final mass remaining at the end of the reaction.



$$\psi = \frac{\Delta \mathrm{Ln}(d\alpha/dt)}{\Delta \mathrm{Ln}(1-\alpha)} \qquad \omega = \frac{\Delta(1/T)}{\Delta \mathrm{Ln}(1-\alpha)}$$

Fig.4: Analysis of the TG data for Iraqi sample by the Freeman-Carroll method eqn.10 .

Fig.3. illustrates typical DTG too.

Fig.4. is a plot of eqn.(10), and shows the data at the heating rate employed.

Values of the kinetic parameters k_0 and E obtained in the present study are $k_0 = 8.8\ 10^{-6} s^{-1}$. $E = 45000$cal/mole with n=0 for temperature between 500 and 870°C.

The kinetic equation for the thermal decomposition of phosphate is

$$k = k_0 \exp(-22727/T)\ \mathrm{mn}^{-1}$$

ISOTHERMAL-THERMOGRAVIMETRY

Fig.5 illustrates the fraction reacted, in the time t for different temperatures.

The expression (2) will be written as

$$\frac{d\alpha}{dt} = k\,\alpha^q \qquad (12)$$

with $f(\alpha) = \alpha^q$ (12)

The integrated function of expression (12) is the form :

$\alpha = kt^n$ (13)

with $q = \frac{n - 1}{n}$

Relation (13) represented in logarithmic co-ordinates give parallel straight lines :

$\log\alpha = \log k + n \log t$ (14)

Straight line slope is very close to unity, thus $\alpha = kt$, $q \approx 0$

Finally, expression (12) will be of the form

$\frac{d\alpha}{dt} = k$ (k rate constant)

On the other hand, the representation in logarithmic co-ordinates of k versus $\frac{1}{T}$ is shown in figure 6. Straight line slope give activation energy $E \approx 45000$ cal.mole^{-1}.

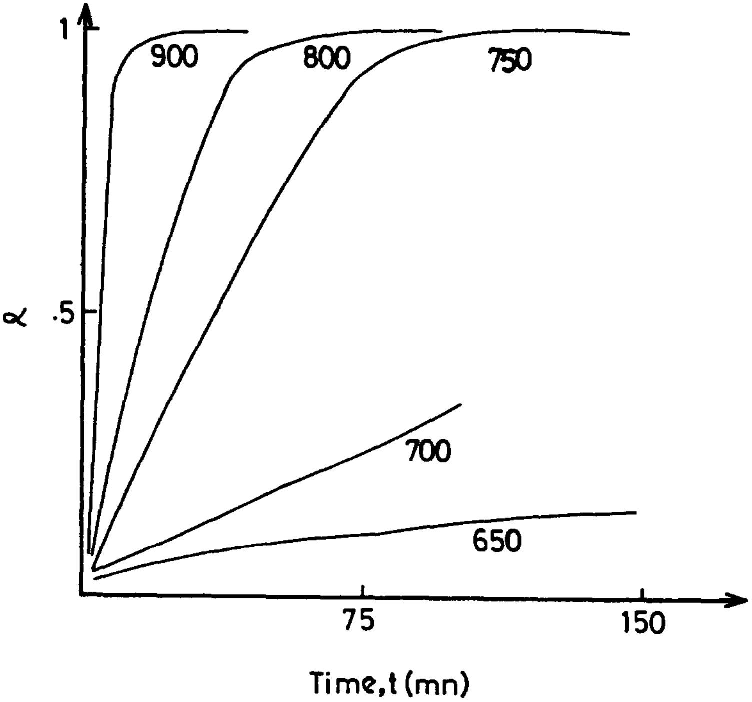


Fig.5: Fractional weight loss α, as a function of time for Iraqi sample at five different temperatures.

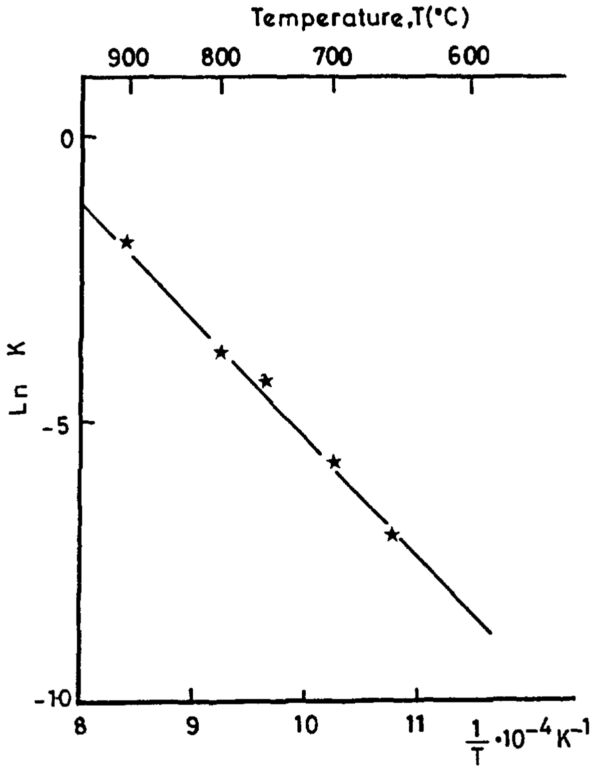


Fig.6: Analysis of the isothermal thermogravimetric data for Iraqi sample by the Freeman- Carroll method.

CONCLUSION

Kinetics of the thermal decomposition of natural Moroccan and Iraqi phosphates have been studied by thermogravimetry.

The kinetic parameters aredetermined from both non-isothermal and isothermal methods.

The particle size 200-315μm is the less carbonated, this result is independent of sweep gas nature used.

The results concerning the activation energy E from non-isothermal method agree with those from isothermal method.

REFERNCES

[1] M.J. MASSON, Rev, Ind. Min. 1959, Vol. 41, n° 8, pp. 651-661
[2] S.M. SMANI, thèse Doctorat ès Sciences, n° A.O. 6892, Nancy, 29 Juin 1973.
[3] A. BRASSENS, Thèse d'Université, n° 314, Université de Nancy I, 26 Juillet 1974.

[4] E. CHOPIN, M. CHRAIBI, A. DAOUDI, Etude cristallochimique de quelques phosphates marocains, B, 1969, T. 49, ler et 2ième semestres.
[5] E.M. BANANE, Thèse 3ième cycle, Université de Perpignan 20 Juillet 1981.
[6] M. ZYOUTE, Thèse 3ième cycle, Faculté des Sciences, Rabat, Decembre 1976.
[7] N.G. W.L., 1975, Aust. S. Chem. 28, pp. 1169-1178.
[8] E.S. FREEMAN et B.J. CARROLL, 1958, J. phys. Chem., 62, p. 394.