Journal of Thermal Analysis and Calorimetry, Vol. 64 (2001) 1247–1255

THERMAL ANALYSIS OF ISRAELI PHOSPHORITES WITH DETERMINATION OF THE EVOLVED GASES

K. Tõnsuaadu, M. Koel and M. Veiderma

Tallinn Technical University, Ehitajate tee 5, Tallinn, 19086, Estonia

Abstract

Thermal analysis of Israeli phosphorites by TG/DTA methods complemented with titrimetric and thermogaschromatographic determination of the evolved gases was performed in an oxygen and inert gas flow. The amounts and temperature intervals of H_2O, CO_2 and SO_2 evolvement were established.

Keywords: evolved gases, Israeli phosphorites, thermal analysis, thermogaschromatography

Introduction

Calcination up to 800–950°C of Israeli phosphorites containing calcite, gypsum, silicates (quartz, opal C–T) in addition to the phosphate mineral (francolite) and some organic matter [1] is used for their beneficiation. The thermal changes occurring during calcination of Israeli phosphorites were investigated by means of FTIR and XRD analyses [2], but some aspects need an additional examination.

Thermal changes in the mixtures of minerals are a complicated subject due to the overlapping thermoeffects and the reactions between the components of the mixture. One of the ways used to resolve these problems is the simultaneous determination of the gases evolved during heating. For this purpose, different analytical techniques are used: titrimetry of the evolved gases (TGT) [3, 4], thermogaschromatography (ThGC) [5, 6], thermogravimetry-mass spectrometry (MS-TG), and thermogravimetry-infrared spectrometry (FTIR-TG).

In this study samples from the Arad and Nahal Zin deposits (Israel) were subjected to thermal analysis by thermogravimetric (TG) and differential thermal analysis (DTA) methods complemented with TGT and ThGC, with the aim to specify the reactions taking place with emission of gases and their temperature intervals during calcination. FTIR and XRD were used for identification of the changes occurring in solid phase.

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Experimental

Materials

Three samples of Israeli phosphorites were studied. Sample 1 from the Arad deposit, sample 2 (bituminous variety) and sample 3 (non-bituminous variety) from the Nahal Zin deposit. The main constituent of the samples is fluorcarbonateapatite. Among the admixtures calcite and organic matter prevail. In sample 3 traces of $CaSO_4$ were also detected. The chemical composition of the samples is shown in Table 1. The samples were ground up to the size of particles less than 200 µm before analyses. For elimination of calcite the initial samples were treated with triammonium citrate (TAC) solution (pH=8) [7]. The dissolution of calcite and $CaSO_4$ was proved by FTIR and XRD analyses.

Table 1 Chemical composition of the samples (mass%)

Sample	1	1*	2	2*	3	3*
P_2O_5	28.2	33.4	29.3	32.3	31.1	36.7
CaO	54.7	51.4	50.6	49.5	53.3	52.8
MgO	0.3	–	0.7	–	0.3	–
Fe_2O_3	0.1	–	0.2	–	0.1	–
Al_2O_3	0.1	–	0.2	–	0.1	–
SiO_2	0.5	–	2.8	–	1.0	–
F	3.3	3.0	2.9	3.2	3.3	3.1
CO_2	10.1	3.9	8.6	3.3	7.7	2.8
SO_3	2.2	–	1.4	–	2.5	–
S^{2-}, ppm	6.0	–	101.1	–	60.8	–
Cl	0.02	–	0.05	–	0.03	–
Org. mat.	0.5	–	2.9	–	0.3	–
Mole ratio CO_2/SO_3	8.4	–	11.4	–	5.6	–

*The samples treated with triammonium citrate solution (pH=8)

Methods

DTA and TG analyses

DTA and TG were determined simultaneously under dynamic condition (10°C min^{-1}) in O_2 or N_2 stream (30 ml min^{-1}) with Setaram LabSys equipment.

Titrimetry of the evolved gases

The temperature regions of emission and the amounts of the evolved CO_2 and SO_2 were determined by the method proposed by Paulik *et al.* [3] with Q-Derivatograph

(MOM) at a heating rate of 5°C min^{-1}, the sample mass was 350–450 mg. The gases were transported into the absorber vessel with a carrier gas (O_2) stream at 10 l h^{-1}. Titration was performed with 0.05 M NaOH solution at pH=4.0 for SO_2 and at pH=9.3 for CO_2. The pH was measured with a glass-calomel electrode.

Thermogaschromatography

The principles of ThGC were described by Küllik *et al.* [6]. The experiments were carried out in the temperature interval from 70 to 600°C at a heating rate of 10°C min^{-1} in an inert atmosphere (He). The evolved gases were analysed with the chromatograph Carlo Erba 4200. The species were separated using a capillary column (NSW-PLOT HNU Nordion, Finland) and detected by a thermal conductivity detector mod.450 HWD and FID. With the PLOT column, due to its limited possibilities (the highest molecular mass organic compounds remaining in the column), information was obtained mostly about the evolution of water, carbon dioxide and light organics.

The sample mass was 20–70 mg. The mass loss of the sample during calcination was measured by weighing the sample before and after heating. The amount of the evolved gases was calculated from the peaks on the thermochromatogram using standards to calibrate the chromatographic detector.

FTIR

FTIR analysis was carried out with a Perkin Elmer 2000 FTIR spectrometer with KBr pellets (3 mg/300 mg KBr).

XRD

XRD analysis was carried out with a DRON-4 Diffractometer using CuK_α radiation at 40 kV, 20 mA. The samples were scanned in the range of 8–60° with a step size 0.04°.

Results and discussion

TG and DTA analyses

The results of DTA and TG analyses are presented in Fig. 1 and Table 2. According to the thermal effects, the curves can be divided into three parts: 20–200, 200–600 and 600–980°C. The mass loss is 0.6–1.2% for all samples at heating up to 200°C.

In the initial samples the mass loss, independently of the atmosphere is 1.2–2.8% at 200–600°C. The differences of the samples and the effect of atmosphere are observed in DTA curves. The exothermic effects with maximums at 300–325 and 350–425°C in oxygen provide evidence of the oxidation of the organic matter. In nitrogen atmosphere the endothermic effect appears at 420–460°C only for bituminous sample 2.

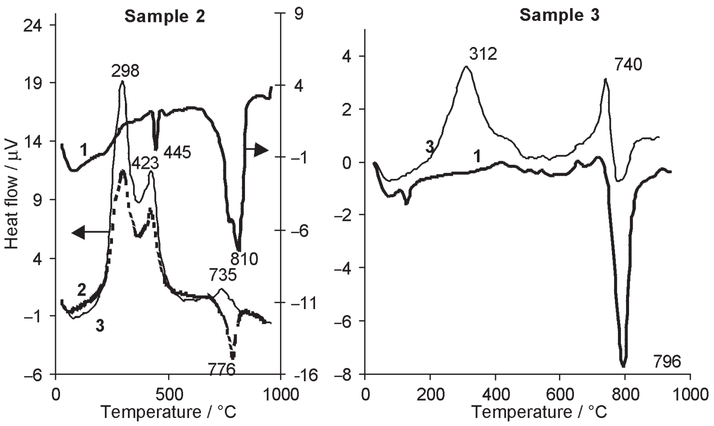

Fig. 1 DTA curves of samples 2 and 3: 1 – initial sample in N_2 flow; 2 – initial sample in O_2 flow; 3 – TAC treated sample in O_2 flow

In the temperature range of 600–980°C the mass loss of the initial samples is almost equal to the content of CO_2 (Tables 1 and 2). In the DTA curves an endothermic effect is seen with a maximum at 790–795°C in O_2 and at 776 and 810°C in N_2 that corresponds to the decomposition of calcite and the emission of CO_2 from the apatite structure. For samples treated with TAC (calcite free samples) an exothermic effect with a maximum at 720–740°C appears and an endothermic effect at 765–800°C follows. These effects are attributed to the changes in apatite structure with emission of CO_2. In the initial sample this was masked by the decomposition of calcite.

ThGC

The results of the ThGC study are presented in Figs 2 and 3 and in Table 3. The detached chromatogram of the evolved products of pyrolysis of the organic matter shows their complicated composition (Fig. 2). Only H_2O and CO_2 were identified and measured, while the existence of light hydrocarbons up to *n*-propane was merely as-

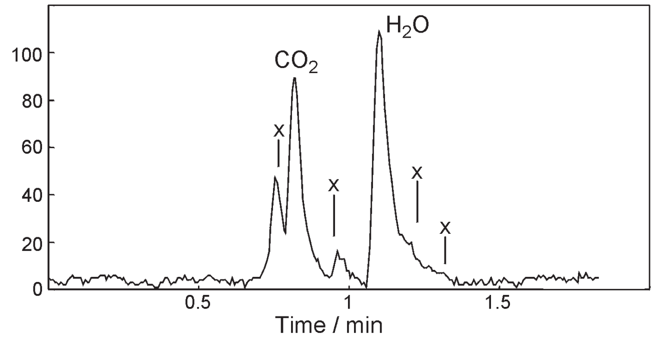

Fig. 2 Chromatogram of the evolved gases from sample 2 at 375°C. X marks unidentified light organic compounds

sumed. As the organic compounds with a higher molecular mass remaining in the column, their direct determination was not possible. Their amount can be approximately calculated from the difference of the mass balance (Table 2). No evolution of H_2S was detected.

Adsorbed water evaporates at 100–160°C. Evolvement of the constitutional water from the minerals and the water from the pyrolysis reactions occurs in a wide temperature interval up to 500°C, with maximums at about 180 and 380–400°C (Fig. 3). This overlaps with the evolvement of CO_2, which is also a product of pyrolysis. The maximum of CO_2 emission is seen at about 350–400°C. The beginning of decomposition of carbonates, particularly of dolomite, causes evolvement of CO_2 at temperatures above 550°C.

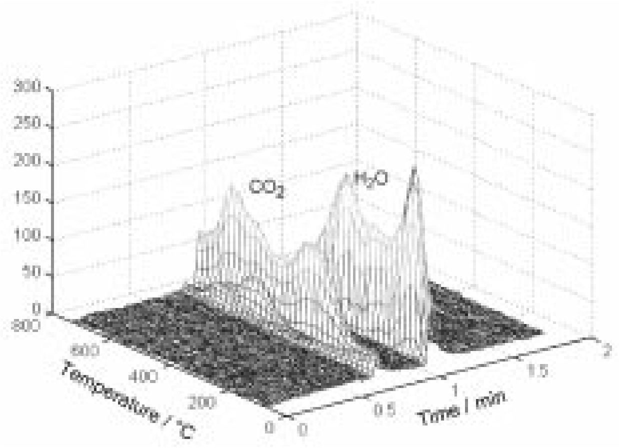

Fig. 3a Thermochromatogram of sample 2

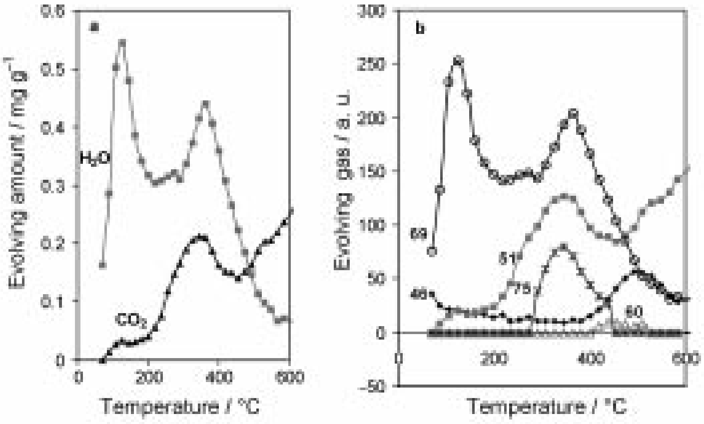

Fig. 3b Amounts of the evolved gases by ThGC of sample 2: a – H_2O and CO_2; b – organic compounds with different retention times (Fig. 2). The numbers indicate the retention time in min

Table 2 The mass loss and amounts of volatile products by TGT in oxygen flow

Sample No.	TG			TGT					
	Mass loss/%			SO_3/%			CO_2/%		
ΔT/°C	20–200	200–600	600–980	20–200	200–600	600–980	20–200	200–600	600–980
1	1.2	2.8	9.8	0	0.10	0.7	0.3	2.4	10.2
2	0.6	2.5	8.1	0	0.05	0	0.8	7.9	9.5
3	1.0	1.2	6.8	0	0.05	2.0	0.05	1.0	4.9

Table 3 The mass loss of the samples and amounts of volatile products by data of ThGC

Sample No.	Mass loss/%				
	Summary	H_2O	CO_2	Light organics	Heavy organics
1	3.0	1.34	0.68	0.81	0.17
2	5.0	0.88	0.52	1.44	2.16
3	5.3	0.87	0.47	0.78	1.18

Because of the limited maximum temperature for ThGC experiment (600°C), estimation of the total amount of the evolving CO_2 and measuring of the other gases evolving at higher temperatures was not possible.

TGT

The results of the TGT analysis are given in Table 2 and Fig. 4. The amount of CO_2 evolved (the gases absorbed at pH=4.0 were subtracted from the gases absorbed at pH=9.3) at 200–600°C in O_2 exceeds the mass loss of sample 2 as a result of the reaction of the organic carbon with oxygen. The mass loss and the mass of the evolved CO_2 are almost equal at 600–980°C, except for sample 3, which has the highest SO_3 content.

Volatilization of SO_2 (gases absorbed at pH=4.0) was observed in samples 1 and 3 (the samples with SO_3 content 2.2 and 2.5%; respectively) at temperatures 780–800°C simultaneously with the evolvement of CO_2. The biggest amount of SO_2 evolves from sample 3 – 77% of the total sulphur content. At temperatures up to 980°C, 34 rel.% of sulphur evolves from sample 1. Sample 2 does not lose any SO_2.

Evolvement of SO_2 is influenced by several factors. By data of earlier studies the temperature interval of SO_2 emission from phosphorites varies from 300 to 900°C, depending on a decomposed sulphur-containing constituent [4]. At 300–500°C sulphur-rich organic matter and at 380–600°C pyrite oxidize, at 800–850°C $MgSO_4$ decomposes. At the same time SO_2 reacts with carbonates and carbonateapatite at temperatures 400–900°C and, as a result, $CaSO_4$ is formed [8, 9]. $CaSO_4$ decomposes above 1200°C. Therefore, the level of SO_2 emission at calcination should depend on the carbonate content in the sample. The amount of SO_2 evolved from the samples studied increases if the mole ratio of CO_2/SO_3 in it decreases (Tables 1 and 2). Thus, the content of carbonates has a significant influence on the evolvement of sulphur from the phosphorites at calcination.

FTIR analysis

The changes in Israeli phosphorites at calcination established by FTIR analysis are:

1. At calcination up to 750°C the organic matter disappears and the amount of CO_3^{2-} substituted into apatite structure and of calcite decreases. By the appearance of the weak peaks at 646, 676, and 1140–1160 cm^{-1} in the spectra, formation of $CaSO_4$ [10] and partial substitution of SO_4^{2-} into apatite structure [11] are assumed to take place.

2. In the spectra of the samples calcined up to 1000°C the bands at 646 and 1144 cm^{-1} attributed to SO_4^{2-} substitution in apatite structure are split up due to a better crystallisation of the sample. The peak of $CaSO_4$ at 676 cm^{-1} is shrinked as a result of the evolvement of SO_2 at temperatures above 750°C (Fig. 4).

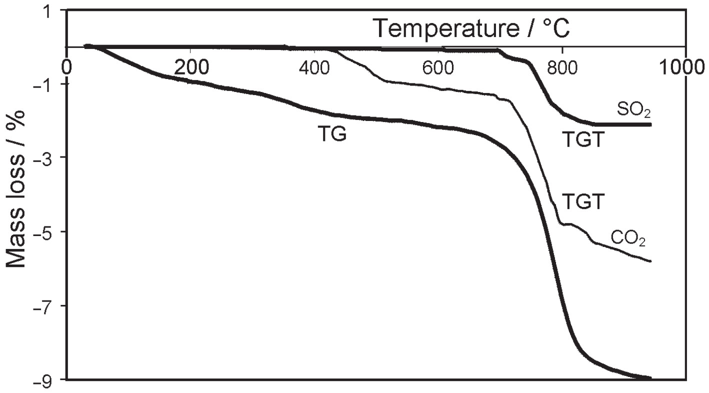

Fig. 4 TG and TGT curves of CO_2 and SO_2 of sample 3

The formation of $CaSO_4$ in the interim stage of calcination and the improvement of crystallinity of apatite was confirmed also by XRD analysis.

Conclusions

By using thermogaschromatography and thermal analysis complemented by titrimetric determination of the evolved gases, we have studied decomposition of the constituent minerals of Israeli phosphorites that occur simultaneously at calcination. H_2O evolves at 80–500, CO_2 mainly in two steps at 200–500 as a result of organic matter oxidation, and at 600–980 as a result of carbonates and carbonateapatite decomposition, and SO_2 above 780°C. Organic compounds volatilize at 250–600°C in an inert atmosphere. The amount of SO_2 evolved depends not only on the sulphur content in a sample but also on the content of carbonates in phosphorite. As a result of calcination not only the carbonates and the organic matter decompose, but changes also occur in the structure of carbonateapatite.

* * *

The authors of the study would like to express their thanks to the Israel Geological Survey for the phosphorite samples they provided, to Mrs. Marve Einard for the chemical analyses performed and to Mrs. Vaike Takjas for participating in the experiments.

References

1 Y. Nathan, Y. Shiloni, R. Roded, J. Gal and Y. Deutsch, Geological Surv. Israel, 73 (1979) 1.
2 R. Knubovets, Y. Nathan, S. Shoval and I. Rabinowitz, J. Thermal Anal., 50 (1997) 229.
3 J. Paulik, F. Paulik and M. Arnold, J. Thermal Anal., 25 (1982) 327.

4 T. Kaljuvee, M. Veiderma, K. Tõnsuaadu and H. Vilbok, J. Thermal Anal., 33 (1988) 839.
5 M. Koel, M. Kudrjashova, K. Tõnsuaadu, M. Peld and M. Veiderma, Thermochim. Acta, 322 (1998) 25.
6 E. Küllik, M. Kaljurand and M. Lamberg, Int. Lab., 17 (1987) 72.
7 S. R. Silverman, R. K. Fuyat and I. D. Weiser, Amer. Miner., 37 (1952) 211.
8 T. Kaljuvee, A. Trikkel and R. Kuusik, Proc. Estonian Acad. Sci., Chem., 43 (1994) 146.
9 K. Tõnsuaadu, M. Peld, V. Bender and M. Veiderma, J. Therm. Anal. Cal., 56 (1999) 35.
10 D. H. Smith and K. S. Seshadri, Spectrochim. Acta, Part A 55 (1999) 795.
11 M. C. Apella and E. J. Baran, Z. Naturf., 34b (1979) 1124.