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THERMAL ANALYSIS OF THE INTERACTION OF PHOSPHORITE WITH CONDENSED PHOSPHATES OF CALCIUM

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The thermal reactions between Maardu (Estonia) phosphorite and acidic phosphates were investigated. TG, DTG and DTA of mixtures with H_3PO_4, $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca_2P_2O_7$ and $[Ca(PO_3)_2]_n$ in different molar ratios showed a maximum mass loss when the $CaO : P_2O_5$ value was 2. The main temperature ranges of the mass losses were determined. The probable reactions relating to the mass losses are given on the basis of the thermal curves and IR spectra.

Addition of phosphoric acid in the hydrothermal treatment of natural phosphates with the object of obtaining fodder material hastens the evolution of fluorine, decreases the temperature of the process and improves the quality of the product [1,2]. According to certain researchers [2–5], partial decomposition of the phosphate rock by phosphoric acid occurs, producing $Ca(H_2PO_4)_2 \cdot H_2O$, and meta and pyrophosphates formed in the heating process interact with the remaining part of the natural phosphate. The lack of more detailed data on the chemism of the process hinders optimization of the process of production of fodder phosphates. To clarify the nature of the possible reactions, we have made thermal investigations of mixtures of phosphorite with phosphoric acid as well as with the compounds assumed to be formed in the reaction between phosphate rock and phosphoric acid. These compounds are $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca_2P_2O_7$ and $[Ca(PO_3)_2]_n$.

The phosphorite originated from Maardu deposits in the Estonian S.S.R. Maardu phosphorite has been formed from the accumulation of phosphate shells of the Obolus and Schmidtia in the coastal zone of the Ordovician Sea [6]. Obolus shells consist mainly (90–95%) of the phosphate mineral fluorcarbonate-apatite with the formula

$$Ca_{9.4}X_{0.6}P_{5.3}C_{0.7}O_{23.3}(OH)_{0.7}F_2$$

where X stands for cations replacing calcium [7]. The mineralogical composition of the remaining part is fairly complex and contains the following components: dolomite, hydroxides of iron, glauconite, feldspar, gypsum, organic matter and pyrite, which appears in a rather dispersed form.

Experimental

Materials

The phosphorite was a flotation concentrate with the chemical composition:

P_2O_5 – 31.41%
CaO – 44.75%
F – 2.99%
CO_2 – 3.90%
R_2O_3 – 2.51%
Fe_2O_3 – 1.95%
SO_3 (in the form of SO_4^{2-}) – 0.59%
SO_3 (in the form of FeS_2) – 3.70%

and sieve characteristics:

$63.4\% < 0.050$ mm
$0.050 \text{ mm} < 13.6\% < 0.071$ mm
$0.071 \text{ mm} < 13.3\% < 0.100$ mm
$0.100 \text{ mm} < 6.1\% < 0.160$ mm
$0.160 \text{ mm} < 3.6\%$

$Ca(H_2PO_4)_2 \cdot H_2O$, $Ca_2P_2O_7$ and $[Ca(PO_3)_2]_n$ were chemical reagents. $Ca_2P_2O_7$ was checked by IR analysis and proved to be γ-$Ca_2P_2O_7$. Mixtures of the phosphorite were made with (a) H_3PO_4, (b) $Ca(H_2PO_4)_2 \cdot H_2O$, (c) $Ca_2P_2O_7$ and (d) $[Ca(PO_3)_2]_n$. Mixtures (b), (c) and (d) were made in an agate mill. A mixture with H_3PO_4 was made in a porcelain mortar, dried at 65° and ground. The compositions of the mixtures were characterized by the Ca/P_2O_5 molar ratio (R), and they were used as air-dried preparations.

Methods

Thermogravimetric, derivative thermogravimetric and differential thermal analytical curves were taken simultaneously by means of a derivatograph (MOM, Budapest). The heating rate was 10°/min. Platinum crucibles were used as sample holders and α-Al_2O_3 was the reference material. Measurements were made in air flowing at 20 l/h. The sample weight was about 900 mg.

Infrared spectra were recorded with Zeiss UR-10 and Perkin-Elmer 421 instruments, using a KBr matrix.

Heated samples were dissolved by means of cation-exchange resin Dowex 50 W. Condensed phosphates were separated by means of paper chromatography, FN-12 paper and Bernhart and Chess [8] solvents were used. Separate forms of phosphates were determined colorimetrically [9].

Results

The thermal curves of the starting compounds are shown in Fig. 1. $Ca(H_2PO_4)_2 \cdot H_2O$ (curve 2) shows three mass loss steps, at 160, 285 and 430°, accompanied by endothermic DTA peaks. The processes are the following [10]:

$$Ca(H_2PO_4)_2 \cdot H_2O \rightarrow Ca(H_2PO_4)_2 + H_2O \qquad (1)$$

$$2\,Ca(H_2PO_4)_2 \rightarrow 2\,Ca(PO_3)_2 + 4\,H_2O \qquad (2)$$

Process (2) takes place in two steps through the evolution of HPO_3 and $Ca_2P_2O_7$. $[Ca(PO_3)_2]_n$ shows a mass loss of only some tenths of a per cent in the investigated temperature range. There is a sharp peak at 975° caused by fusion. The DTA curve of $Ca_2P_2O_7$ shows no thermal effects.

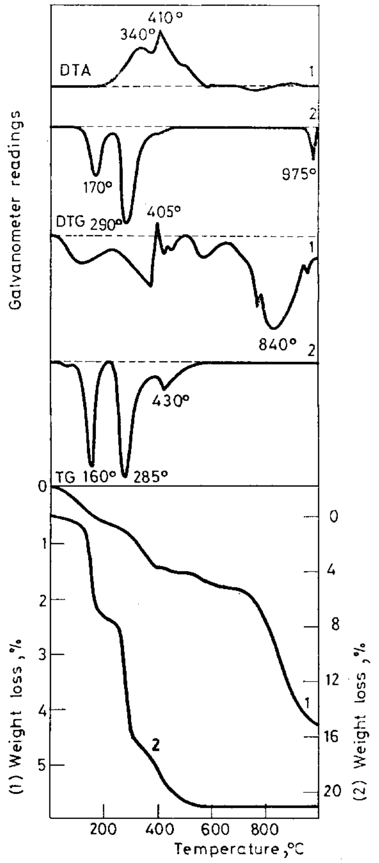

Fig. 1. 1-Maardu phosphorite; 2-$Ca(H_2PO_4)_2 \cdot H_2O$

The TG curve of phosphorite (curve 1) shows a small mass loss from below 100° to about 220°, due to the escape of differently bound water. The subsequent, more pronounced steps up to 500° are of exothermic character. The oxidation of organic matter takes place in this temperature range. A mass increase at 405° is caused by a small pyrite content.

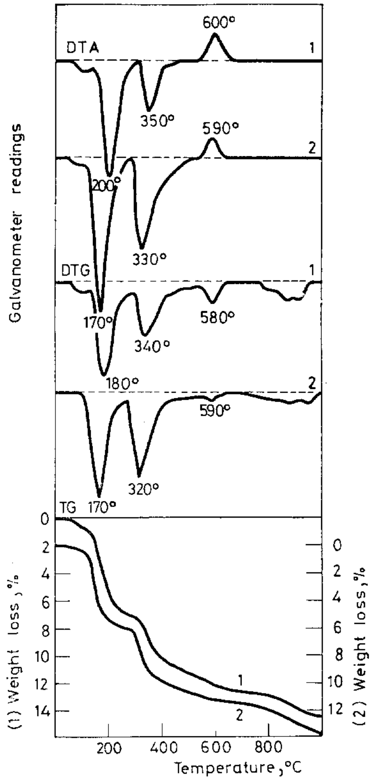

Fig. 2. 1-Phosphorite + H_3PO_4, $R = 2.0$; 2-Phosphorite + $Ca(H_2PO_4)_2 \cdot H_2O$, $R = 2.0$

The mass loss is less than 2% up to 680° and amounts to another 2% up to 980°. In the second range the carbonate moiety decomposes. According to the IR spectrum of the original substance, the carbonate is present in the form of CO_3^{2-} ions replacing PO_4^{3-} ions in the fluorapatite crystals. The IR spectra of phosphorite heated up to 720° and to 1000° prove the evolution of CO_2 in this temperature range.

The thermal curves of the mixtures of phosphorite with H_3PO_4 or $Ca(H_2PO_4) \cdot H_2O$ at $R = 2.0$ (Fig. 2) are similar to that of $Ca(H_2PO_4) \cdot H_2O$, except that dehydration seems to be completed at 460°, that is approximately 40° before that of pure $Ca(H_2PO_4) \cdot H_2O$. However, there is a characteristic exothermic

DTA peak in both curves at around 590° that cannot be observed with either phosphorite or $Ca(H_2PO_4)_2 \cdot H_2O$ alone. Therefore, this peak may be considered a sign of the reaction between phosphorite and the dehydration products of $Ca(H_2PO_4)_2$. From the rather similar DTG and DTA curves of the two mixtures, the formation of $Ca(H_2PO_4)_2 \cdot H_2O$ in the mixture with H_3PO_4 is assumed. At the same time, the DTG peak at around 430°, observable in the curve for pure $Ca(H_2PO_4) \cdot H_2O$ (Fig. 1, curve 2), is lacking from the curves of the mixtures.

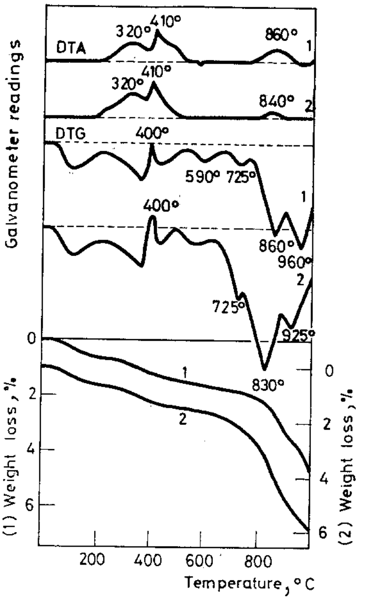

Fig. 3. 1-Phosphorite + $Ca_2P_2O_7$, $R = 3.0$; 2-Phosphorite + $Ca(PO_3)_2$, $R = 3.0$

This may be explained by the fact that during the second step of dehydration the evolved HPO_3 reacts to yield water that evaporates from the pure salt, while the reaction product of HPO_3 and phosphorite does not escape in the same temperature range.

In the mixture with H_3PO_4 the reaction proceeds with greater loss of mass at 590° than in the mixture with $Ca(H_2PO_4)_2 \cdot H_2O$. It can be concluded from this that at this temperature the dehydration products of free H_3PO_4 react with phosphorite. This conclusion is confirmed by the presence of free acid in the mixture with H_3PO_4 treated at 500°, and its absence from the mixture treated at 650°.

Thermal curves of the mixtures with $Ca_2P_2O_7$ and with $[Ca(PO_3)_2]_n$ are shown in Figs 3 and 4. Judging from the DTG and TG curves in the high temperature range (Fig. 3), the main mass loss begins at 800° in the mixture with $Ca_2P_2O_7$, but in mixtures with $[Ca(PO_3)_2]_n$ it does so at 650°. In mixtures with $Ca_2P_2O_7$

(R = 3.0) the reaction proceeds in two steps, at 800–900° and above 900°. With $[Ca(PO_3)_2]_n$ (Fig. 4) the shape of the DTG curve depends on the value of R: at R = 2.0 three stages, at R = 2.6 two stages, and at R = 3.0 three stages could be observed. As only small sensitivities could be used with the mixture of H_3PO_4, because of dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$, and as the thermal curves of this mixture are not comparable with those of mixtures with $Ca_2P_2O_7$ and $[Ca(PO_3)_2]_n$, the mixture with H_3PO_4 was investigated by derivatograph twice. First the mixture was heated up to 450°, until $Ca(H_2PO_4)_2 \cdot H_2O$ was completely dehydrated, and after this heating was repeated at a higher sensitivity up to 1000°. From Fig. 4 (the second parts of the thermal curves are given) it can be seen that for this mixture in the temperature range 650–1000° changes analogous to those of mixtures with $[Ca(PO_3)_2]_n$ take place. Since different mixtures contain different quantities of phosphorite, which when heated also show a loss of mass, for the

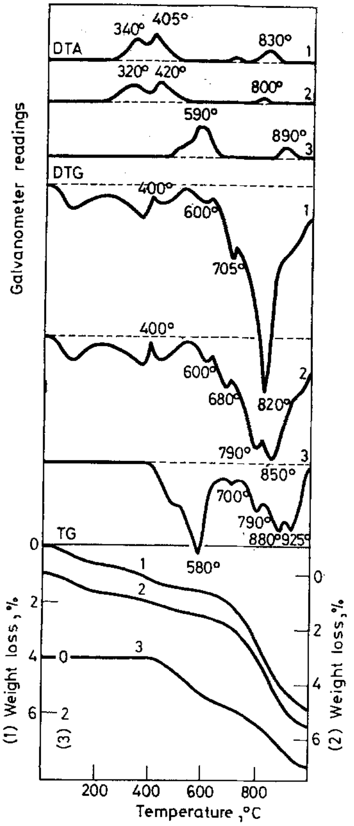

Fig. 4. 1-Phosphorite + $Ca(PO_3)_2$, $R = 2.6$; 2-Phosphorite + $Ca(PO_3)_2$, $R = 2.0$; 3-Phosphorite + H_3PO_4, $R = 2.0$, investigated derivatographically after heating up to 450°

Table 1

Mass loss of various phosphorite charges on heating from 500° to 1000°

Charge	R	Mass loss, %	Phosphorite content in charge, %	Mass loss related to phosphorite mass, %
Maardu phosphorite		2.80	100.0	2.80
Phosphorite-H_3PO_4	2.0	2.76	48.6	5.73
Phosphorite-$Ca(H_2PO_4)$ · · H_2O	2.0	3.00	52.5	5.72
Phosphorite-$[Ca(PO_3)_2]$	2.0	4.17	58.7	7.12
Phosphorite-$[Ca(PO_3)_2]_n$	2.6	4.48	76.5	5.86
Phosphorite-$[Ca(PO_3)_2]_n$	3.0	4.64	87.9	5.28
Phosphorite-$Ca_2P_2O_7$	3.0	3.39	73.9	4.58

characterization of the interaction we plotted the change of mass of the mixture with respect to the mass of phosphorite (Table 1). In connection with the fact that dehydration and polymerization of phosphates is completed at 460–500°, the loss of mass was calculated in the temperature range 500–1000°. The results show that in all mixtures investigated the reactions proceed with a mass loss exceeding that of the original phosphorite. The similarity of the processes in mixtures with H_3PO_4 and with $Ca(H_2PO_4)_2 \cdot H_2O$ is also revealed by the similar mass losses of the two mixtures.

For the determination of the temperatures at which the reactions proceed, the changes in mass of the mixtures were calculated along the TG curve after every 20°. The mass losses related to the mass loss of the pure phosphorite contained in the mixture were plotted as a function of the temperature (Fig. 5).

From the results in Fig. 5 it can be concluded that reactions involving a loss of mass in the mixture of phosphorite and $[Ca(PO_3)_2]_n$ begin at 400° and proceed with greater rate at 420–440°, 520–530°, 680–700°, 750–760°, 860–880° and above 920°, but in mixtures with $Ca_2P_2O_7$ the principal reactions proceed at 420°, 520° and above 920°. The IR spectrum of the phosphorite-$[Ca(PO_3)_2]_n$ mixture shows no significant change up to 560° compared to the spectra of the pure components. Above 720° $P_2O_7^{4-}$ appears and at 950° pure β-$Ca_2P_2O_7$ remains. In the mixture with $Ca_2P_2O_7$, β-$Ca_3(PO_4)_2$ appears at about 800°. Thus, $[Ca(PO_3)_2]_n$ and $Ca_2P_2O_7$ begin to react with phosphorite at about 700° and 800°. Peaks at 420–530° are caused by differences in decomposition of the pyrite in the mixtures.

In the mixture with H_3PO_4 the determination of the beginning of the reaction is rather difficult because of the dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$. Reactions proceed efficiently at 520–590° and at 660–700°, but somewhat less efficiently at 740° and 940–960°. In the mixture with $Ca(H_2PO_4)_2 \cdot H_2O$ reactions are generally analogous to those in the mixture with H_3PO_4, with the exception of the reaction at 590°, which is nearly absent. The IR spectrum of the dried phosphorite-H_3PO_4 mixture shows the characteristics of phosphorite and of $Ca(H_2PO_4)_2 \cdot H_2O$. In the spectrum of the mixture heated up to 390° (that is, to about the end of the second stage of the TG curve), the presence of $P_2O_7^{4-}$ can be detected at 710 cm^{-1}. The mixture contains γ-$Ca_2P_2O_7$ from 450° on. (In pure $Ca(H_2PO_4)_2 \cdot H_2O$ at the same temperature PO_3^{2-} is present.) Above 780° the appearance of peaks at 1200–1300 cm^{-1} (not yet fully explained) indicates further reactions. At the same time a peak at 775 cm^{-1} shows the presence of the P–F bond [11]. At 950° the peaks at 775 cm^{-1} and 1200–1300 cm^{-1} disappear, and the end-product contains β-$Ca_2P_2O_7$. Chromatographic analysis also shows a rise in the content of $P_2O_7^{4-}$ in a mixture with H_3PO_4 heated above 390°. Mixtures heated up to 390°, 490°, 650° and 950° contain 28.9%, 39.6%, 52.5% and 80.4% P_2O_5 from the total in the form of $P_2O_4^{7-}$. Proceeding from the composition of the products of dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ [12], the content of $P_2O_7^{4-}$ at 390° must be 1.15%, while at 490° and above it is lacking. Hence, the presence of $P_2O_7^{4-}$ here is not caused by the dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$; it is rather the product of reaction between phosphorite and condensed phosphates. From these results it can be concluded that lower polyphosphates (formed by thermal dehydration of $Ca(H_2PO_4)_2 \cdot H_2O$ at 390°) have far higher reactivities than $[Ca(PO_3)_2]_n$.

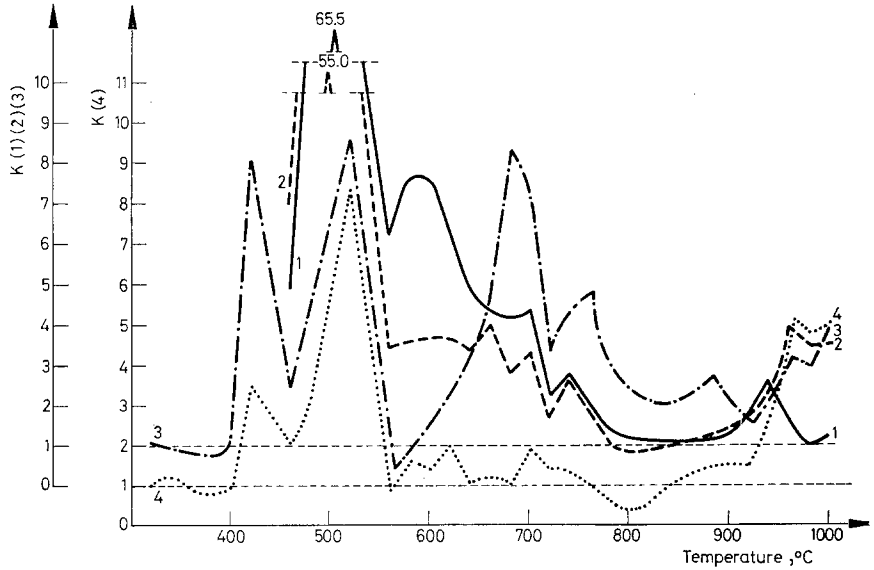

Fig. 5. Relative loss of mass in various charges. 1-Maardu phosphorite-H_3PO_4, $R = 2.0$; 2-Maardu phosphorite-$Ca(H_2PO_4)_2 \cdot H_2O$, $R = 2.0$; 3-phosphorite-$Ca(PO_3)_2$, $R = 2.0$; 4-phosphorite-$Ca_2P_2O_7$, $R = 3.0$.

$$K = \frac{\text{Mass loss of charge related to the mass of phosph. \%}}{\text{Mass loss of phosphorite, \%}}$$

Comparing relative mass losses of different mixtures, one can see that with all these mixtures there are reactions proceeding in the same temperature ranges (620–720° and above 900°). However, there are also certain differences in these curves (no reactions at 560° in mixtures with $[Ca(PO_3)_2]_n$ and $Ca_2P_2O_7$, and reaction at 750–760° in mixtures with $[Ca(PO_3)_2]_n$, etc.). A more precise determination of the chemism of these reactions and the causes of the established differences is the immediate task of subsequent research.

Thus, the investigations carried out here have proved that phosphorite reacts with condensed phosphates on heating, and have given information indispensable for the exact determination of the chemism of the process of acidic-thermal treatment of phosphate rock.

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Résumé — Etude de l'effet thermique lié à la réaction entre la phosphorite de Maardu (Estonie) et les hydrogénophosphates. Etude par TG, TGD et ATD de mélanges de H_3PO_4 avec $Ca(H_2PO_4)_2 \cdot 2\,H_2O$, $Ca_2P_2O_7$ et $[Ca(PO_3)_2]_n$ réalisés avec différents rapports molaires; mise en évidence d'une perte de masse maximale pour le rapport $CaO : P_2O_5$ égal à deux. Détermination des principaux domaines de température où s'effectuent les pertes de masse. On donne les réactions probables correspondant aux pertes de masse en s'appuyant sur les courbes d'analyse thermique et spectres infrarouges.

ZUSAMMENFASSUNG — Die thermische Reaktion zwischen Phosphorit aus Maardu (Estnien) und sauren Phosphaten wurde untersucht. TG, DTG und DTA von Gemischen mit H_3PO_4, $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca_2P_2O_7$ und $[Ca(PO_3)_2]_n$ in verschiedenen molaren Verhältnissen zeigten den größten Massenverlust bei dem Verhältnis von $CaO : P_2O_5 = 2$. Die wichtigsten Temperaturbereiche der Massenverluste wurden bestimmt. Die den Massenverlusten zugeordneten wahrscheinlichen Reaktionen werden aus den erhaltenen thermischen Kurven und IR Spektren ermittelt.

Резюме — Исследована термическая реакция между маардуским фосфоритом (Эстония) и кислыми фосфатами. TG, DTG и DTA смесей с H_3PO_4, $Ca(H_2PO_4)_2 \cdot H_2O$, $Ca_2P_2O_7$ и $[Ca(PO_3)_2]_n$ в различных молярных соотношениях показали максимум потери веса, когда соотношение $CaO : P_2O_5$ было равно 2. Определены главные температурные области потери веса. На основании термических кривых приведены возможные реакции, которые коррелируются с потерей веса.