

INVESTIGATIONS OF THE THERMAL STABILITY AND PHASE TRANSFORMATIONS IN THE SYSTEM MAROCCO PHOSPHORITE – $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4$

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Abstract

Different physical chemical methods were used to study the thermochemical processes in a system involving a natural phosphate and complex acid salts of ammonium sulphate.

The products of decomposition of the double ammonium salt and the products of their interactions with the phosphate were identified. The formation of ammonium and calcium polyphosphates and the disproportionation of $\text{P}_3\text{O}_{10}^{5-}$ and $\text{P}_2\text{O}_7^{4-}$ to PO_4^{3-} and PO_3^- were found to depend on the circumstances of the thermal interactions.

Keywords: double ammonium salt, phase transition, thermal stability

Introduction

Ammonium sulphate and its complex acid salts present in the waste solutions from methyl methacrylate production can be regarded as a nitrogen and sulphur-containing raw material for the decomposition of natural phosphates to obtain mineral fertilizers. If the thermal decomposition takes place in a suitable temperature range, the final products will contain ammonium phosphates.

Hussen and Aglan [1, 2] have described general variations in mixtures of natural phosphate and NH_4HSO_4 without any attempt to elaborate on the observed changes. Data have been reported on the thermal stability and decomposition of natural phosphates with $[(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4]$ [4]. The influence of temperature on the thermal processes occurring in mixtures of Marocco phosphate and $(\text{NH}_4)_2\text{SO}_4$ [3] are of interesting in research involving thermal treatment of the system Marocco phosphorite $\text{NH}_4\text{HSO}_4 \cdot (\text{NH}_4)_3\text{H}(\text{SO}_4)_2$.

The present work relates to an investigation of the thermal stability and phase changes in the system Marocco phosphorite – $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4$.

Experimental

The investigations were carried out with phosphorite with a P_2O_5 content of 33.9%. The second reagent, containing N, was a mixture of $(NH_4)_3H(SO_4)_2$ and NH_4HSO_4 , obtained via the reaction:



An X-ray phase breakdown of the obtained salt is shown in Fig. 1. The initial content of N was 16.03%, as determined by the method of Kjeldahl. A mole ratio $N:P_2O_5 = 1:1$ in the initial mixtures was used.

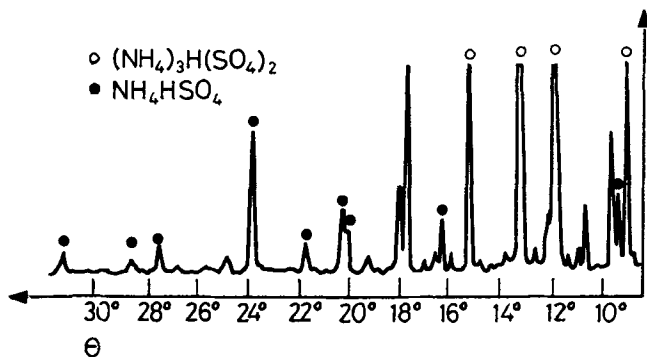


Fig. 1 RPA of product containing $(NH_4)_3H(SO_4)_2$ and NH_4HSO_4

The thermal treatment carried out in the temperature range 573–873 K, with an isothermal heating regime and a reaction time of 60 min. The soluble and total P_2O_5 contents were determined by standard calorimetric methods. The soluble P_2O_5 was extracted with Peterman's solution. The contents of polyphosphate forms which break down in this extractant to $[PO_4^{3-}]$ are obtained directly as $[P_2O_5^*]$, and those polyphosphates whose (POP) chains are not broken in Peterman's solution are determined after their hydrolysis with 10 ml 25% HCl. Differential thermal breakdown analysis (DTA) was performed on a Q-1500D, derivatograph at a heating rate of 10 deg/min. Infrared spectra (IRS) were recorded on a Specord apparatus, by using standard KBr pills. X-ray phase analysis (RPA) was carried out with radiation from a standard Cu-cathode. Transmission electron microscopy (TEM) and the electronograms (ETA) of some samples involved use of a Philips electron microscope in the direct control regime.

Results and discussion

The processes which occur under the influence of temperature in the system phosphate – $[\text{NH}_4\text{HSO}_4 \cdot (\text{NH}_4)_3\text{H}(\text{SO}_4)_2]$ are reflected by the DTA of a sample from this system (Figs 2 and 3). The endothermic effect (Fig. 2) at 393 K cor-

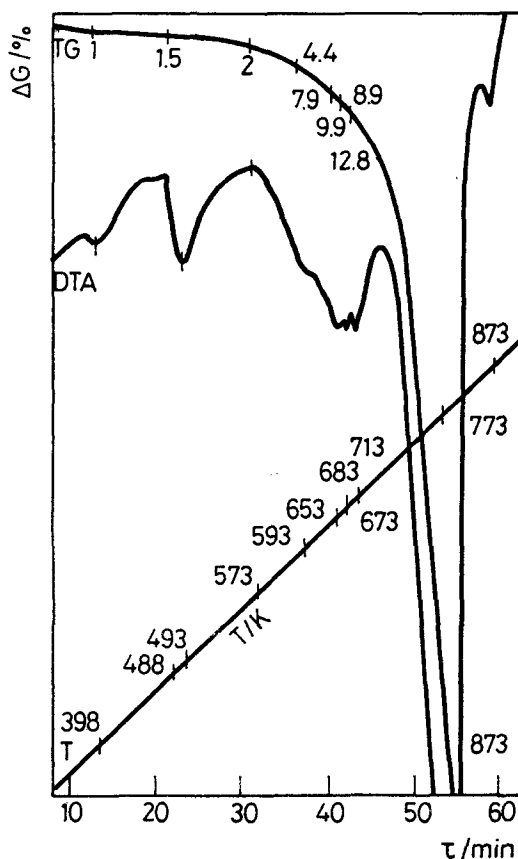
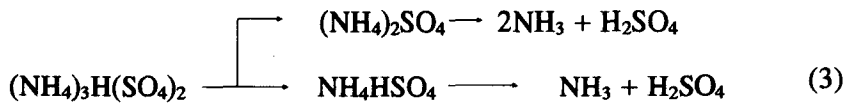


Fig. 2 DTA of product containing $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ and NH_4HSO_4

responds to the melting of NH_4HSO_4 , and that at 488 K to the melting of the complex salt. The processes of thermal decomposition of NH_4HSO_4 and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ begin at 573 K according to reactions 2 and 3:



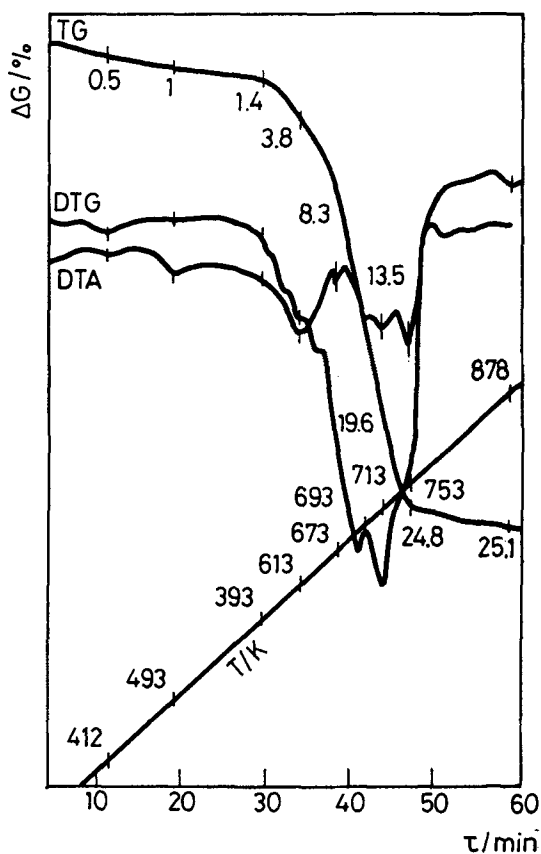


Fig. 3 DTA of mixture of Marocco phosphorite and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4$

The triplet of endoeffects (Fig. 2) in the range 653–683 K describes the decomposition of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ in accordance with the mechanism of reactions 2 and 3. The H_2SO_4 produced decomposes at 773 K, giving a strong endoeffect, with which the decomposition of the pair of salts is completed. The DTA curve for the phosphorite mixture with $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4$ (Fig. 3) in the low-temperature region is analogous with the curve $\text{NH}_4\text{HSO}_4 \cdot (\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ (Fig. 2). NH_4HSO_4 melting is observed at 412 K, and the melting of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ at 439 K. The chemical interactions of these two salts with phosphate are possible in the melt state as confirmed by the new endoeffects. The RPA of the solid phase proved the presence of ammonium di- and triphosphates, the respective calcium salts, and reacted phosphorite and CaSO_4 . The presence of the polyphosphate forms was confirmed by the IR spectrum, in which the bands at 760 and 1160 cm^{-1} and the peak at 1108 cm^{-1} relate to $\text{P}_2\text{O}_7^{4-}$, and those at 1280 and

1180 cm^{-1} and 870 cm^{-1} to $\text{P}_3\text{O}_{10}^{5-}$ (Fig. 5). Chemical analysis gave $\text{P}_2\text{O}_5^*/\text{P}_2\text{O}_5 \text{ sol} = 77.3\%$ (Table 1), which is further proof of the considerable changes in the structure and composition of the mixture.

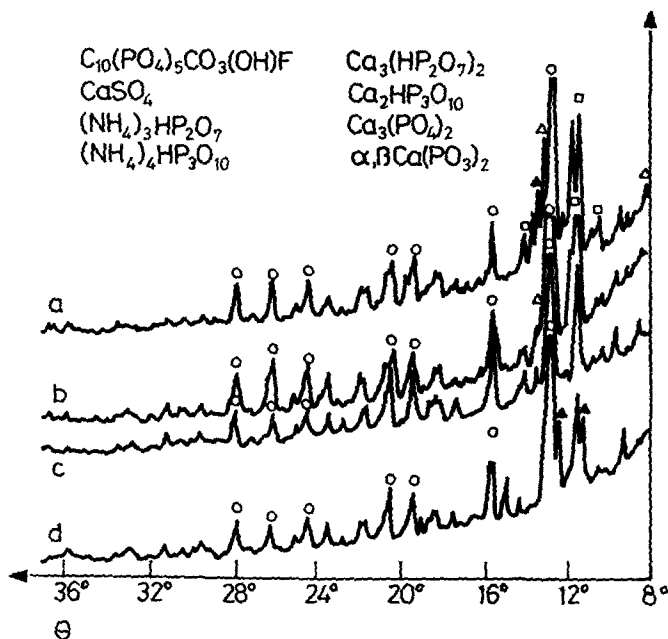


Fig. 4 RPA of thermally treated mixture of Morocco phosphorite and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4$: a - 573 K; b - 623 K; c - 673 K; d - 723 K

Table 1 Ratios $\text{P}_2\text{O}_5^*/\text{P}_2\text{O}_5 \text{ sol}$ in the products of thermal treatment of mixtures of Morocco phosphorite and $\text{NH}_4\text{HSO}_4 \cdot (\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ at different temperatures

$T /$ K	$\text{P}_2\text{O}_5 \text{ sol}$ %	$\text{P}_2\text{O}_5 \text{ abs}$ %	P_2O_5^* %	$\text{P}_2\text{O}_5^*/\text{P}_2\text{O}_5 \text{ sol}$ %
573	11.15	5.10	8.10	73.3
623	11.45	5.70	8.79	77.4
673	13.0	5.71	11.19	85.8
723	20.1	5.28	14.48	72.0
773	20.5	5.16	14.80	72.4
823	20.9	4.92	16.34	78.3
873	21.4	4.24	16.76	78.3

The thermal decomposition of the acid ammonium phosphates and of the unreacted NH_4HSO_4 begins at 593 K (Fig. 3), and is accompanied by a dramatic

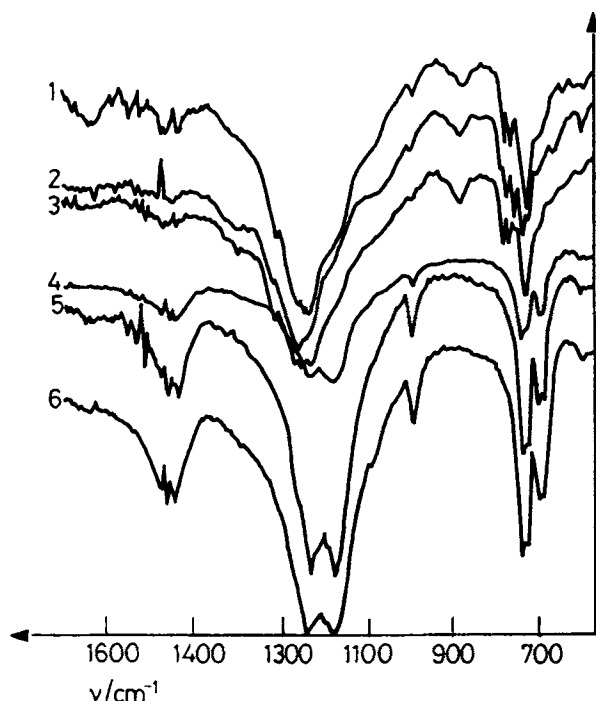


Fig.5 IRS of thermally treated mixture of Morocco phosphorite and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4$: 1 - 573 K; 2 - 623 K; 3 - 673 K; 4 - 723 K; 5 - 773 K; 6 - 823 K

decrease in mass. The X-ray spectrum shows no features characteristic of $(\text{NH}_4)_3\text{HP}_2\text{O}_7$ or $(\text{NH}_4)_4\text{HP}_3\text{O}_{10}$ (Fig. 4b). The increase in the ratio $\text{P}_2\text{O}_5^*/\text{P}_2\text{O}_5$ sol suggests that $\text{HP}_2\text{O}_7^{3-}$ and $\text{HP}_3\text{O}_{10}^{4-}$ from the ammonium hydrogenphosphates were converted to $\text{Ca}_3(\text{HP}_2\text{O}_7)_2$ and $\text{Ca}_2\text{HP}_3\text{O}_{10}$. The IR spectrum of the sample heated at 623 K is identical with that of the sample treated at 673 K (Figs 5–2, 3). At this temperature, the DTA curve (Fig. 3) shows a small endoeffect, initially observed in the decomposition of the melt of $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$ according to reaction 3. The process is accompanied by a mass loss of 8.3%. The ratio $\text{P}_2\text{O}_5^*/\text{P}_2\text{O}_5$ sol increases 85.8%, a possible reason being the complete conversion of the acid ammonium di- and triphosphates to the relevant calcium phosphates. In the temperature range 693–713 K, the DTA curves reveal the recovery of two peaks, showing the consecutive decomposition reactions of $\text{Ca}_3(\text{HP}_2\text{O}_7)_2$ and $\text{Ca}_2\text{HP}_3\text{O}_{10}$, accompanied by mass losses of 19.6%. The thermal decomposition of these salts is connected with processes of disproportionation of $\text{P}_3\text{O}_{10}^{5-}$ and $\text{P}_2\text{O}_7^{4-}$ to PO_4^{3-} and PO_3^- . This effect is clearly reflected by the IR spectrum (Fig. 5), with bands characterizing the PO_4^{3-} ion at 568, 607, 1095, 1100 and 1420 cm^{-1} , and the characteristic spec-

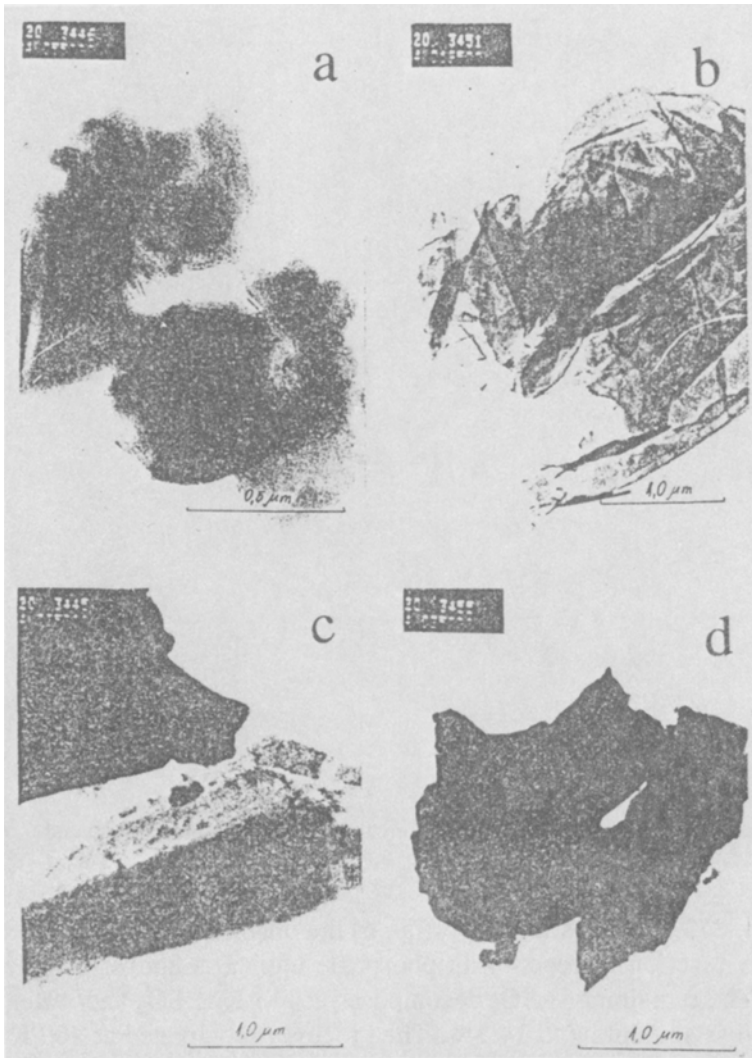


Fig. 6 EM photographs of thermally treated mixture of phosphorite and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4$: a - 723 K; b - 723 K; c - 773 K; d - 823 K

trum of $\text{PO}_3^- : \nu_s^{\text{PO}_2}$ at 1180 and 1115 cm^{-1} , and $\nu_{\text{as}}^{\text{POP}}$ at 1050 and 940 cm^{-1} . The X-ray spectrum (Fig. 4b) displays features characteristic of $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}(\text{PO}_3)_2$. The chemical analysis show a considerable decrease in the ratio $\text{P}_2\text{O}_5^*/\text{P}_2\text{O}_5 \text{ sol}$, due to the poor ability of Peterman's solution to extract phosphates with a non-chain and noncyclic structure. The shortage of the characteristic peaks of natural phosphate in the X-ray spectra of samples obtained at 723 K, and the weak increase in the ratio $\text{P}_2\text{O}_5^*/\text{P}_2\text{O}_5 \text{ sol}$ in the temperature

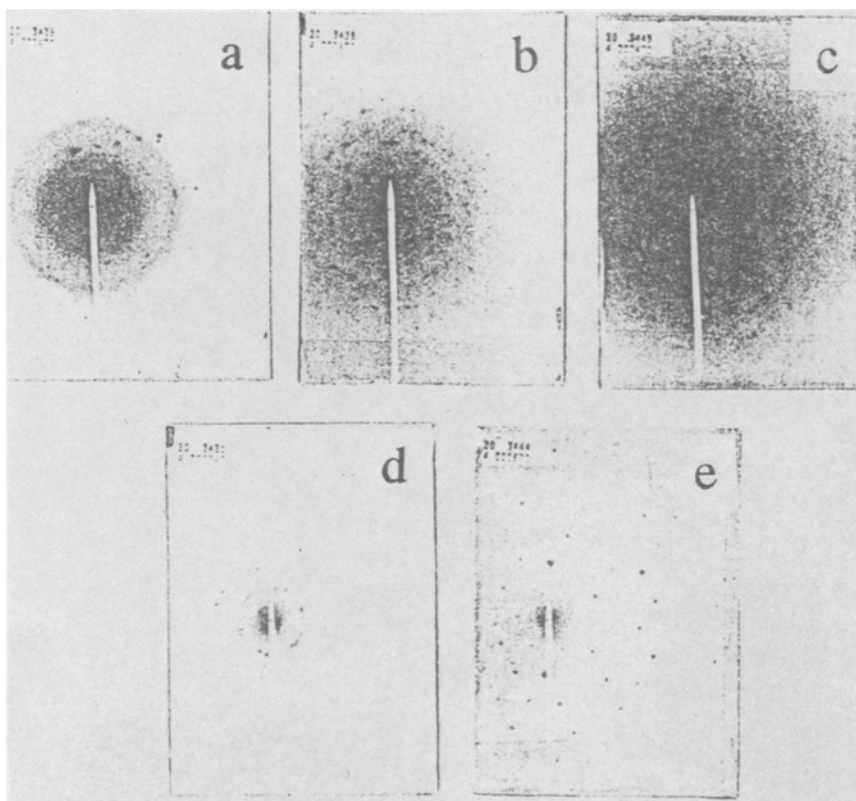


Fig. 7 Electronograms of thermally treated mixture of Morocco phosphorite and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2 \cdot \text{NH}_4\text{HSO}_4$: a - 723 K; b - 723 K; c - 773 K; d - 773 K; e - 873 K

range 723–873 K, shows that a portion of the uncombined H_2SO_4 formed (according to reaction 3) reacts with phosphate until it is almost completely exhausted. The remaining H_2SO_4 decomposes at 713 K to SO_3 and water vapour, the mass loss amounting to 14.8%. The process is completed at 800 K.

For confirmation of the described phase changes in the investigated transmission electron microscopy was used as an independent method. In the direct observation regime, the sample obtained at 723 K (Fig. 6a, b) is a sinter of several phases with not very well-defined forms. There is a section of liquid phase H_2SO_4 , which sublimes (from the temperature of the electronic sheaf), at which the field of the trial decreases. The electronograms of the separate sections provided by these samples (Fig. 7a, b) indicate different types of crystal structures (Table 2).

In the electronogram, the polycrystalline structure with hexagonal syngony predominates, proving the presence of unreacted natural phosphate. The sam-

ples obtained at 773 K (Fig. 6c) demonstrate asymmetric forms with a marked aptitude for aggregation, at which their electronic transparency decreases. The electronograms (Fig. 7c, d) directly confirm the changes. Pseudocrystal forms were obtained whose polymorphism displays features characterizing a crystal lattice, and not with concentric circumferences, a phenomenon observed for the samples obtained at 873 K (Fig. 7e). Direct observation (Fig. 6d) reveals strongly aggregated crystal phases which are electronographically non-transparent. The intersurface distance (*d*) taken from the electronograms proves the existence of the phases determined by RPA (Table 2).

Table 2 RPA and TEM of mixtures thermally treated at 573, 623, 673, 723, 773 and 823 K

	RPA	TEM
$\text{Ca}_{10}(\text{PO}_4)_3\text{CO}_3(\text{OH})\text{F}$	2.717; 2.81; 2.26; 2.77 x 1.94; 1.81	2.723; 2.80; 2.27 x 1.93
CaSO_4AXII	3.49; 2.85; 2.32; 2.20 x 1.74; 1.64; 1.38; 1.28	3.50; 2.81; --; 2.18 x 1.60; 1.32; --; 1.19
$\text{Ca}_3(\text{HP}_2\text{O}_7)_2$	3.81; 3.41; 3.15; 2.89 x x 2.77; 5.43; 4.93; 3.77	3.87; 3.43; --; 2.7 x x 5.39; 4.91; -
b $\text{Ca}_3(\text{PO}_4)_2$	2.88; 2.61; 3.21; 3.45 x 1.71	2.72; 2.68; 3.19; 3.4 x
b $\text{Ca}(\text{PO}_3)_2$	3.49; 2.76; 4.76; 4.18 x 3.02; 3.61	3.50; 2.72; 4.69; --; x 3.00; 3.57
$\text{Ca}(\text{PO}_3)_2$	3.74; 3.52; 4.58; 4.23 x x 3.17; 2.85; 3.30; 3.01	3.71; 3.50; 4.49; --; x x 4.19; 3.04; 3.80

Conclusion

The experimental results and their analysis permit the following conclusions:

1. In the temperature range 573–873 K, a thermochemical interaction occurs between the thermally stable natural phosphate and the unstable double ammonium salt, during which different ammonium and calcium polyphosphates are obtained as proved by DTA, RPA, IRS, TEM, ETA and chemical analyses.

2. The results of the different methods used proved the stability of the phosphate up to 873 K; decomposition of the double ammonium salt to NH_3 , NH_4HSO_4 , $(\text{NH}_4)_2\text{SO}_4$, and H_2SO_4 and the formation of a melt, the formation of diammonium phosphate, triammonium phosphate and calcium phosphates at 439 K; the decomposition at 593 K of acid ammonium phosphates and the formation of $\text{Ca}_3(\text{HP}_2\text{O}_7)_2$ and $\text{Ca}_2\text{HP}_3\text{O}_{10}$, and in the range 693–713 K the decomposition of the latter to $\text{Ca}_3(\text{PO}_4)_2$ and $\text{Ca}(\text{PO}_3)_2$.

3. The stage of decomposition of the ammonium salts, the chemical mechanism of their interaction with the natural phosphate and the rates of the thermal chemical processes all depend on the circumstances of the thermal treatment.

References

- 1 M. Hussen, CEER, 1979, v.II, NII, 47–49.
- 2 M. Hussen and S. Aglan, CEER, 1979, v.II, NII, 49–51.
- 3 I. Dombalov and M. Arasheva, Chem. Ind., 3 (1982) 29.
- 4 A. Y. Tavrovskaya, A. Podleskaya and N. Portnova, Trudi NIUIF, vip.240, Moskva, 1982, p.169–170.
- 5 M. E. Posin, Technologia mineralnich solei, Goschimisdat, Leningrad, 1961, p.685–689.

Zusammenfassung — Verschiedene physikalische Methoden wurden zur Untersuchung thermochemischer Prozesse in einem System mit natürlichen Phosphaten und komplexen sauren Salzen von Ammoniumsulfat angewendet.

Die Produkte der Zersetzung der Doppelammoniumsalze und die Produkte ihrer Wechselwirkung mit den Phosphaten wurden identifiziert.

Man fand die Bildung von Ammonium- und Calciumphosphaten und die Disproportionierung von $\text{P}_3\text{O}_{10}^{5-}$ und $\text{P}_2\text{O}_7^{4-}$ zu PO_4^{3-} und PO_3^- , je nach den Umständen der thermischen Wechselwirkung.