

# Structural Transformations Accompanying Mechanochemical Activation of Natural Phosphorite from Syria

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## Abstract

The effect of mechanochemical activation (MCA) on the structure and properties of Syrian phosphorite is investigated. The character of structural changes and their effect on the solubility of activated Syrian phosphorite are studied with the help of X-ray phase analysis, infrared and electron spectroscopy, and thermal analysis. It is established that MCA causes substantial structural perturbations in the initial phosphorite; they result in an increase in the reactivity and solubility of mechanochemically activated phosphorite samples.

## INTRODUCTION

Numerous publications deal with mechanochemical activation (MCA) of natural phosphates and prove the possibility of almost complete transformation of phosphorus into assimilable forms as a result of the application of mechanochemical method to process natural phosphates in order to obtain mineral fertilizers [1–4]. An increase in the content of assimilable phosphorus forms and an increase in the reactivity of phosphates are explained by structural changes occurring as a result of mechanical action [1–4]. Mechanical activation involves such transformations as mechanolysis of  $\text{CaCO}_3$  and  $\text{Ca}_3\text{F}(\text{PO}_4)_2$ . The most important result is a substantial increase in the content of assimilable forms of phosphorus in mechanically activated phosphate [4–9].

Syrian phosphorite is one of the most widely used phosphorites. Nevertheless, changes occurring in the structure of Syrian phosphorite under the conditions of MCA are not so thoroughly investigated.

The goal of the present communication is investigation of the character of structural changes using X-ray phase analysis (XPA), infrared spectroscopy (IRS), electron microscopy (EM) and thermal analysis (TA) and their effect on the solubility of the activated Syrian phosphorite.

## EXPERIMENTAL

Syrian phosphorite of the following composition was used in the investigation: mass concentration, %:  $\text{P}_2\text{O}_5$  (total) 29.5,  $\text{P}_2\text{O}_5$  (c. s.) 6.9, F 3.2, CaO 46.5,  $\text{R}_2\text{O}_3$  (R = Al, Fe) 0.55,  $\text{SO}_3$  1.1,  $\text{SiO}_2$  7.3, MgO 0.35, Cl 0.05,  $\text{CO}_2$  6.2, moisture content 3.14 %; mean granulometric composition of particles: 0.08 mm.

Mechanochemical activation of Syrian phosphorite was carried out in Pulverizette-5 planetary mill (Fritsch company, Germany) at a rate of  $320 \text{ min}^{-1}$ , activation time was 30–300 min, milling bodies (MB) were made of chromium-nickel steel, MB mass was 400 g,

the number of MB was 100, the diameter of MB was 10 mm, mass of the samples for mechanochemical activation was 20 g.

The degree of transformation of non-assimilable forms into assimilable ones was estimated on the basis of the content of  $P_2O_5$  soluble in the solutions of 2% citric acid and ammonium citrate (pH 7) according to the Bulgarian State Standard 13418-80.

The X-ray phase analysis was carried out with DRON diffractometer ( $CuK_{\alpha}$  radiation). The degree of phosphorite amorphization was determined on the basis of XPA data using equation  $A_m = 100 - K$ , where  $K = 100(I_{MA}/I_{init})$  is the degree of crystallinity;  $I_{MA}$  and  $I_{init}$  are the intensities of the main reflections of mechanically activated and initial samples, respectively [1]. The structure of the initial Syrian phosphorite is quite crystal, it does not contain amorphous phase. Amorphization degree of apatite was estimated as an arithmetic mean of the sum of intensities of three reflections with interplanar spacings  $d = 2.78, 2.69, 2.62 \text{ \AA}$ .

Experiments on TG, DTG and DTA were carried out using Stanton Redcroft thermoanalytical complex (England) within temperature range 20–1400 K with the heating rate of 10 K/min in the gas medium (air). The mass of samples was  $(15 \pm 0.3) \text{ mg}$ .

Investigations by means of electron microscopy were carried out with a scanning electron microscope PHOLOPS PH, SEM 515 model under the conditions of secondary electron emission.

## RESULTS AND DISCUSSION

### Results of solubility measurements

Non-treated Syrian phosphorite is characterized by the solubility ( $P_2O_5$  (assim.)/ $P_2O_5$  (tot.), %) in citrate ammonium solutions equal to 11.2, in citric acid 23.5. Changes in the solubility of mechanically activated samples of Syrian phosphorite are shown in Fig. 1. One can see that the solubility increases rapidly with an increase in activation time, which is especially noticeable in the case of ammonium citrate, and reaches its maximum for activation time of 165 min. An increase in activation time leads

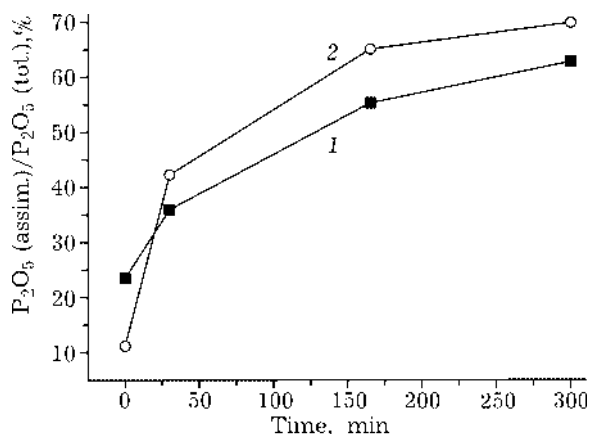


Fig. 1. Dependence of the solubility of Syrian phosphorite on the duration of mechanochemical activation in solutions: 1 - 2% citric acid, 2 - ammonium citrate (pH 7).

to the establishment of a steady state, which was also observed by other authors [1].

With an increase in activation time (to 165 min), a rapid increase in amorphization degree is observed; it is followed by slowing down and establishment of constant values (Fig. 2). There is no direct correlation between solubility and amorphization degree. Solubility in 2% solution of citric acid is due to local structural defects of fluoroapatite on the prismatic  $\{3030\}$  and pyramidal  $\{1231\}$  planes and is determined by distortions of the short-range order in apatite lattice. The solubility of phosphorite in the solution of ammonium citrate depends on the types of defects, their localization, and the degree of stoichiometry Ca/P [1, 11]; it

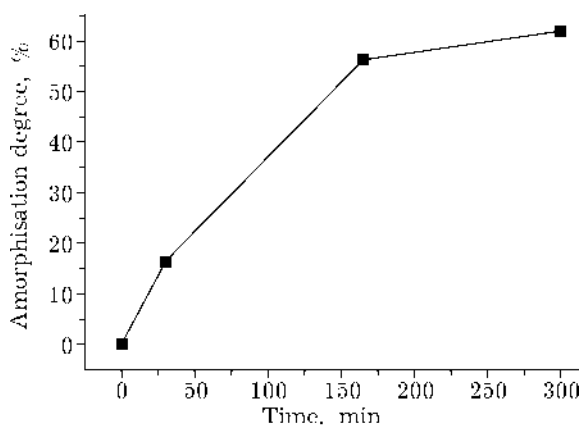


Fig. 2. Dependence of amorphization degree of Syrian phosphorite on the duration of mechanochemical activation.

TABLE 1

The data of X-ray phase analysis of the samples of Syrian phosphorite (SP)

SP sample	Identified phases
Initial	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> - 4.04, 3.83, 3.42, 3.18, 2.78, 2.68, 2.62, 2.49, 2.27, 2.23, 2.11, 2.05, 1.92, 1.87, 1.83, 1.79, 1.75, 1.72, 1.63, 1.46, 1.45, 1.42 SiO <sub>2</sub> - 4.25, 3.32, 1.81 β-Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> - 5.27, 4.07, 3.42, 3.01, 2.89, 2.60, 2.01, 1.93 CaCO <sub>3</sub> - 3.83, 3.03, 2.49, 2.28, 2.10, 1.90, 1.85
Activated for, min:	
30	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> , SiO <sub>2</sub> , CaCO <sub>3</sub> , Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> · xH <sub>2</sub> O - 3.47, 2.83, 2.72, 1.95, 1.85 Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 2H <sub>2</sub> O - 3.01, 2.61, 2.45, 2.27, 2.10, 1.89
165	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> , SiO <sub>2</sub> , CaCO <sub>3</sub> , Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> · xH <sub>2</sub> O, Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 2H <sub>2</sub> O
300	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> , SiO <sub>2</sub> , Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> · xH <sub>2</sub> O, Ca <sub>2</sub> P <sub>2</sub> O <sub>7</sub> · 2H <sub>2</sub> O

increases for Ca/P > 1.67 (for Syrian phosphorite Ca/P = 1.69) and with an increase in MCA time. After long MCA we observe an increase in the number of defects in the sublattice of the complex anion, that is, substitutions in PO<sub>4</sub> group, which causes distortions of the long-range order in the crystal structure of apatite. Dissolution in ammonium citrate proceeds mainly over the basis plane (0002).

An increase in the solubility in the solution of ammonium citrate and an increase in amorphization degree (see Figs. 1, 2) in these experiments is defined by the time of MCA and provides evidence of deep perturbations occurring in the structure of Syrian phosphorite during MCA, which results in an increase in the reactivity of activated samples.

### Results of physicochemical analyses

It seems important to investigate changes in solubility depending on structural distortions of the activated Syrian phosphorite. Changes in the diffraction patterns of reflections of the main phases (and the appearance of the new ones) (Fig. 3, Table 1) and crystallinity of samples in electron microscopic images (Fig. 4) may provide indirect evidence of the degree of defect content of the crystal structure depending on activation time. When comparing the diffraction patterns of non-activated phosphorite with

those for activated samples, a trend to reflection broadening and a decrease in the intensity of reflections was established. This is most clearly exhibited for the main triplet of calcium fluoroapatite (2.78 Å, 2.69 Å, 2.62 Å). The recorded changes in the reflections of diffraction patterns of activated samples provide evidence of an increase in amorphization degree and distortions of a three-dimensional periodicity of the structure. The same is confirmed by electron microscopic investigations providing the most clear evidence of a decrease in crystallite size and the disappearance of the characteristic crystal appearance of the samples (see Fig. 4). In addition to structural changes, the results of XPA indicate the presence of reflections of two new phases: Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> · xH<sub>2</sub>O and Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> · xH<sub>2</sub>O, where x = 2. The presence of these two compounds in the solid product after activation proves the occurrence of solid-phase synthesis.

The presence of carbonate group plays a substantial role in distortions of the crystal structure. The presence of calcite is established in the diffraction patterns of the initial phosphorite on the basis of the most intensive reflections (d = 3.03, 3.86, 2.49 Å) which disappear during activation (see Fig. 3, Table 1). This gives us reasons to state that MCA involves mechanolysis of free carbonates, which

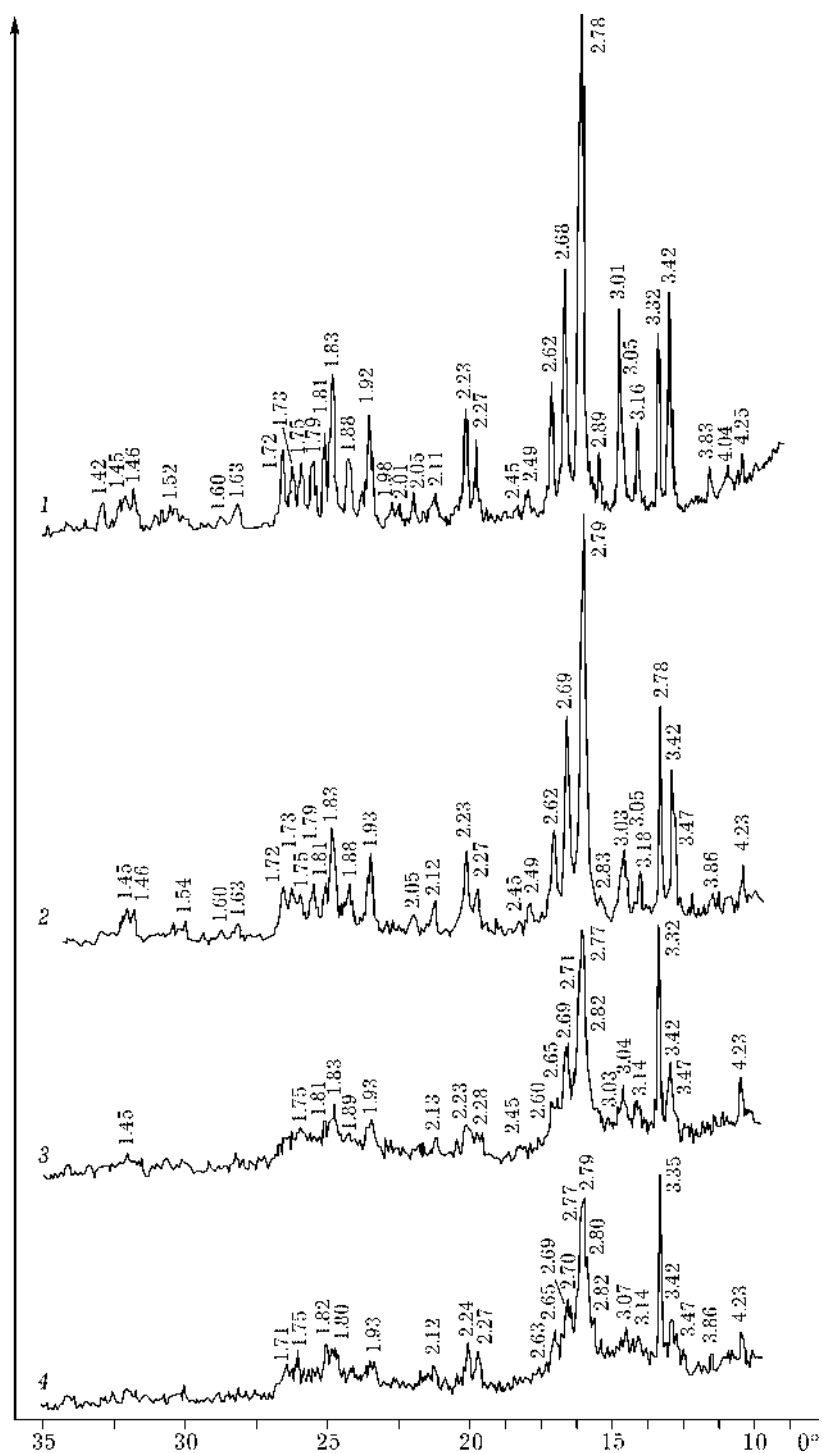


Fig. 3. Diffraction patterns of the samples of Syrian phosphorite: 1 – initial, 2–4 – mechanochemically activated for 30 (2), 150 (3) and 300 min (4).

promotes an increase in the solubility of activated samples.

The results of IR investigation of the activated samples provide evidence of deep structural perturbations during MCA. Mechanochemical activation causes changes in

the vibration bands of the main functional groups of phosphorite –  $\text{PO}_4^{3-}$ ,  $\text{CO}_3^{2-}$  and  $\text{OH}^-$  (Fig. 5), we observe broadening of the stretching bands of  $\text{PO}_4^{3-}$  at the frequency of  $1045\text{ cm}^{-1}$ ; such a broadening is typical for MCA. After activation for 30 min, the intensity of

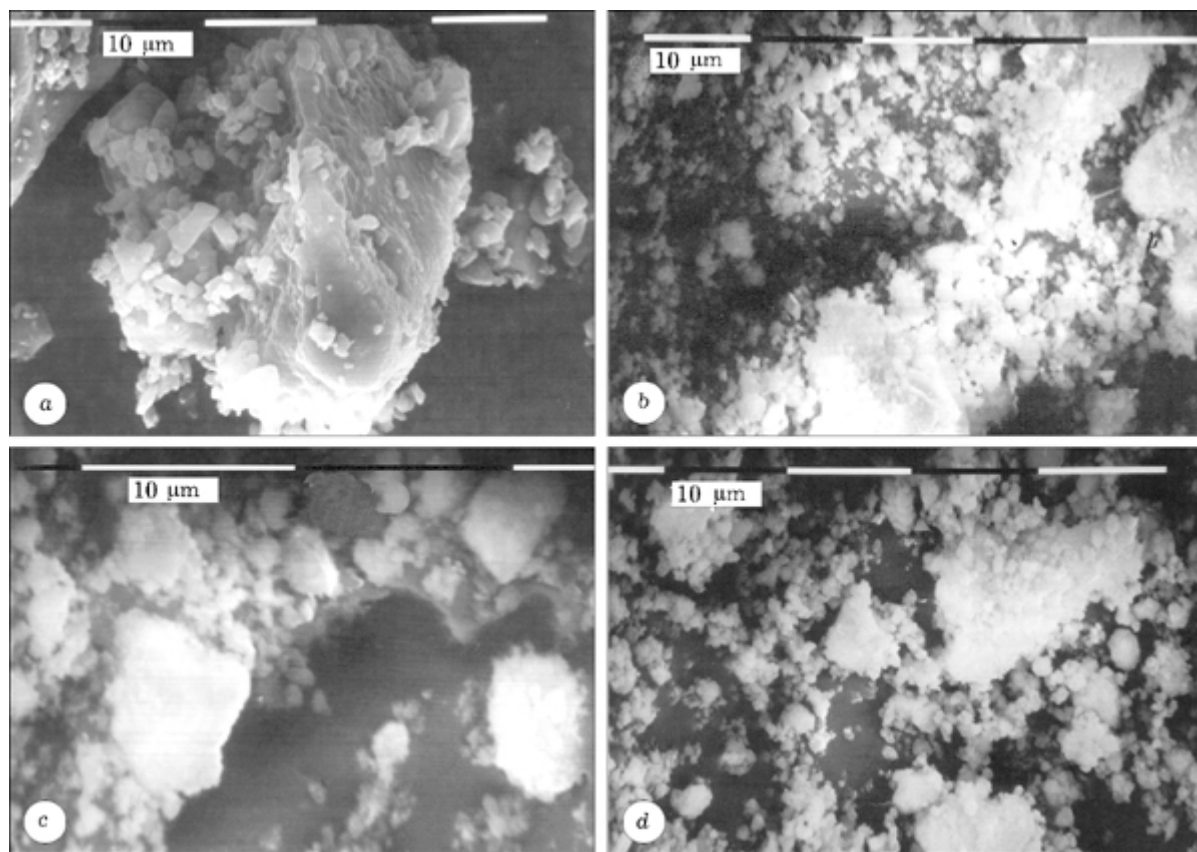


Fig. 4. Electron microscopic images of the samples of Syrian phosphorite: *a* – initial, *b–d* – mechanochemically activated for 30 (*b*), 165 (*c*) and 300 min (*d*).

the band at the frequency of  $\nu_1(\text{PO}_4^{3-}) = 970 \text{ cm}^{-1}$  decreases, and a trend to its disappearance is observed. These facts confirm perturbations of the short-range order. The active surface of the phosphorite increases during activation, and new surfaces appear [11]. This results in the acceleration and enhancement of the degree of bonding water vapour from the air; this is clearly observed for the structurally bound  $\text{OH}^-$  ion ( $d = 1650 \text{ cm}^{-1}$ ). With an increase in activation time, the intensities of bands  $\nu_3(\text{CO}_3) = 1435 \text{ cm}^{-1}$  and  $\nu_3(\text{CO}_3) = 1460 \text{ cm}^{-1}$  increase. A new band appears at  $\nu_3(\text{CO}_3) = 1515 \text{ cm}^{-1}$ , which is likely to be related to insertion of  $\text{CO}_3^{2-}$  into the sites of structural perturbations in the activated samples [8]. After activation for 165 min, the width of vibrational bands increases and their intensity decreases. The shift of the band of stretching vibrations of  $\text{CO}_3^{2-}$  to higher frequency confirms the conclusions of some other researchers [1, 11] that the presence of carbonates causes profound distortions of

phosphorite structure due to insertion of  $\text{CO}_3^{2-}$  into the vacancies of phosphate tetrahedron and the channels of the structure. This fact may also explain an increase in the solubility of activated samples in the solutions of ammonium citrate. After MCA, the bands characteristic of  $\text{P}_2\text{O}_7^{2-}$  ion appear in the IR spectra ( $\nu_s(\text{P-O-P}) = 685, 775 \text{ cm}^{-1}$ ;  $\nu_s(\text{PO}_3) = 990 \text{ cm}^{-1}$  and  $\nu_{\text{as}}(\text{PO}_3) = 1140 \text{ cm}^{-1}$ ); this confirms the results of XPA.

The results obtained by means of XPA, IRS and EM confirm the possibility of the formation of phosphate ion chains which are exhibited in the case under consideration as the formation of the crystal hydrate of  $\text{Ca}_2\text{P}_2\text{O}_7$  in activated phosphate samples. The formation of  $\text{P}_2\text{O}_7^{2-}$  groups under the action of the accumulated mechanical energy, taking into account the distribution of these groups in the phosphorite structure, is likely to be the most profitable process from the energy point of view.

The presence of  $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$  and  $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  in the form of crystal hydrates

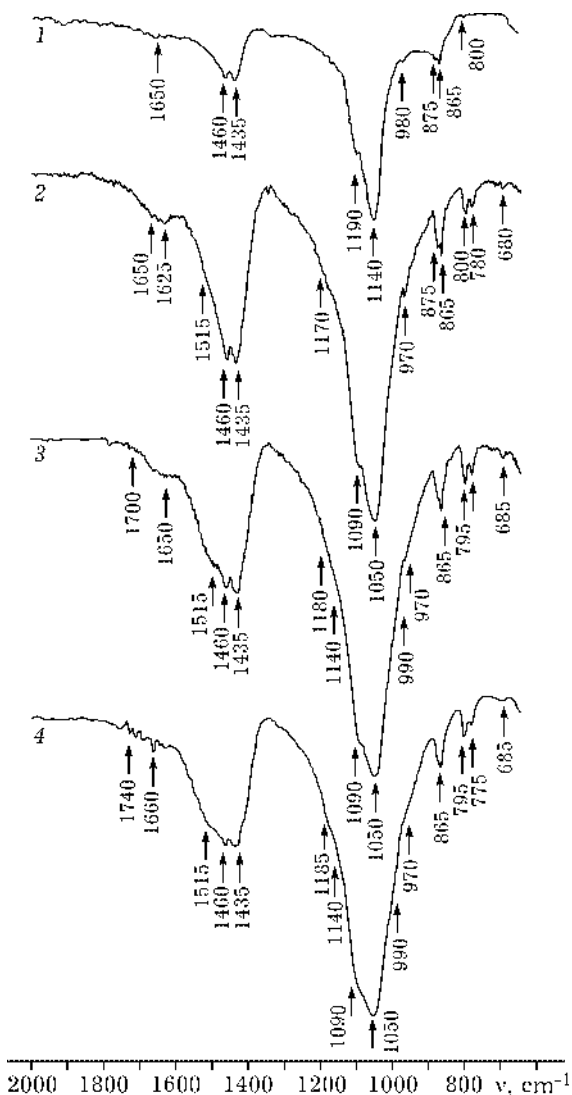
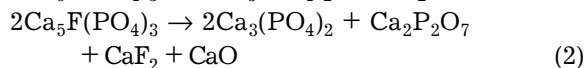


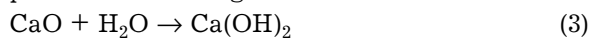
Fig. 5. IR spectra of the samples of Syrian phosphorite: 1 – initial, 2–4 – mechanochemically activated for 30 (2), 165 (3) and 300 min (4).

in the spectra of XPA and in IRS is explained by the absorption of water vapour from the air after MCA of the samples.

The chemical nature of the processes that most likely occur during activation can be represented by the following reactions:



Calcium oxide is likely to interact with water vapour and  $\text{CO}_2$  from the air forming the side products according to reactions



The presence of diffraction lines of  $\text{Ca}_2\text{P}_2\text{O}_7$  and  $\text{Ca}_3(\text{PO}_4)_2$  in the form of crystal hydrates

in the solid products after MCA confirms the assumed reaction mechanism. It may also be assumed that the compounds obtained during MCA have the structure characterized by high defect content and non-stoichiometric composition. They are likely to have different solubility than that of the analogues of those compounds in the pure form. This assumption may be confirmed by the results on the solubility in the solutions of citric acid and ammonium citrate, as well as by the recorded decrease in the intensities of reflections in the diffraction patterns of samples after MCA.

### Results of thermal analysis

The results on heating the non-activated and activated Syrian phosphorite samples within the temperature range up to 1400 K under the dynamic mode of heating are shown in Fig. 6. The adsorbed water evolves from the apatite structure within a broad temperature range: 373–783 K;  $\text{CO}_3^{2-}$  evolves above 893 K. Mass losses (5.9 %) observed during heating of the initial Syrian phosphorite to 1117.5 K are explained by the release of crystal and physically bound water, decarbonization of  $\text{CO}_2$  bound in the phosphorite structure, and carbonates. The analysis of TG, DTA, DTG dependencies of the activated samples indicates an increase in mass loss (see Fig. 6). At the same time, a new endothermic effect is recorded within temperature range 350–666 K, which is due to dehydration of  $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$  and  $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$  obtained during activation. An increase in mass loss to 3.1 % (see Fig. 6, b) within this range provides evidence of an increase in the amount of these compounds with activation time. For transformation intervals corresponding to the non-activated and activated samples, a decrease in temperature by 20–50 K is observed; this is most clearly exhibited for thermal transformations within the range below 980 K. This proves that MCA intensifies phosphorite decomposition process. The recorded endothermic effects within temperature range 830–1025 K can be explained by the evolution of  $\text{CO}_2$ , which is weaker bound in the phosphorite structure, while within the range 1023–1170 K the reason is evolution of

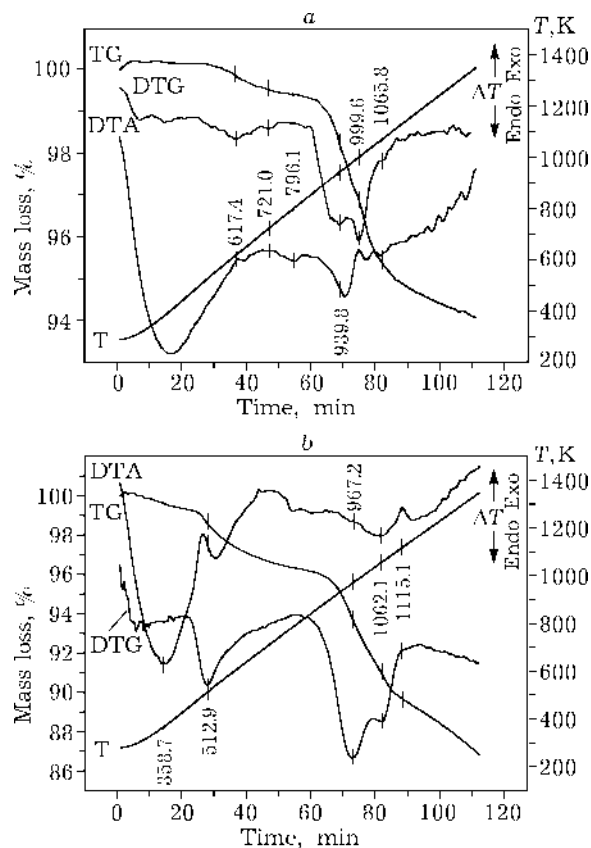


Fig. 6. TG, DTG, DTA and T dependencies of the samples of Syrian phosphorite: 1 – initial, 2 – mechanochemically activated for 300 min.

the residual  $\text{CO}_3^{2-}$  [1]. The demonstrated increase in mass loss within temperature ranges 830–1023 K (to 4.3 %) and 1023–1170 K (to 2.6 %) once more confirms the assumption that insertion of  $\text{CO}_3^{2-}$  into the phosphate structure and the formation of new amounts of free carbonates occur during MCA.

When the activated sample is heated for up to 300 min within temperature range 1023.7–1168.9 K, a combination of endothermic and exothermic peaks is observed (see Fig. 6, b). The exothermic peak is absent for thermal decomposition of non-activated phosphorite (see Fig. 6, a). The appearance of an endothermic peak is explained by thermal decomposition of free carbonates. The obtained data correspond to the results obtained in [1] for structural and phase transformations that occur in apatite–calcite–quartz system in the case when calcite taken in excess. The results of thermal decomposition of activated Syrian phosphorite can be related to the same system because the

Syrian phosphorite belongs to the second group of alkaline phosphates (according to the structural chemical classification proposed by M. V. Chaikina), for which  $(\text{Ca}/\text{P})_{\text{at}} > 1.67$  (1.80–1.90). The exothermal effect can be interpreted in two ways: on the one hand, by recrystallization of calcium silicate obtained during heating [1], on the other hand, by relaxation of the accumulated mechanical energy. Its release involves spontaneous restructuring of the solid phase and the formation of energetically stable system.

The data of physicochemical methods and thermal analysis show that MCA results in profound perturbation of the crystal structure, insertion of carbonate and hydroxyl groups for the compensation of defects in the structure, and the formation of new compounds with defect-bearing structure. The manifestation of defect content is an increase in the reactivity and solubility of mechanically activated samples of Syrian phosphorite.

## CONCLUSIONS

The results obtained in the investigation give us reasons to make the following conclusions:

1. The results of physicochemical methods and thermal analysis show substantial changes in the structure of the initial phosphorite during MCA. These changes are connected with the insertion of water vapour and carbon dioxide into the sites with structural perturbations, which renders irreversible character to these changes.

2. As a result of distortions of crystal structure, the solubility of activated samples of Syrian phosphorite in the solution of ammonium citrate increases substantially.

Thus, we may state that selecting the conditions of MCA one may obtain Syrian phosphorite without acidic treatment; this phosphorite will be suitable for direct use as a phosphorus-containing fertilizer.

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