

## MECHANICAL ACTIVATION OF SYRIAN PHOSPHORITE

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**Abstract.** The structural changes and the phase transformations in Syrian phosphorite subjected to tribochemical activation in a planet mill with chrome nickel steel milling bodies have been studied in the present paper. The thermal and spectroscopic analyses show some considerable changes in the structure of the initial phosphorite due to the process of tribochemical activation. These changes are accompanied by the introduction of water and carbon dioxide to areas with structural violations which facilitates their stabilisation. As a result of the occurred changes the content of the assimilated forms of phosphorus in the activated phosphorite is increased. This gives us the reason to assume that under suitable conditions of mechanical activation Syrian phosphorite can be used as a phosphorus fertiliser.

**Keywords:** activation, tribochemical, phosphorite.

### AIMS AND BACKGROUND

The main aims of organic agriculture is to preserve permanently the soil fertility and the environment. For this purpose, special cares are laid to decrease the food loss and it is recommended to apply slowly acting fertilisers. One of the areas actively explored is the tribochemical activation of the natural phosphates aiming at transforming them into phosphorous, long-lasting fertilisers<sup>1-6</sup>. Among the most used phosphorites, the changes occurring with Syrian phosphorite in the conditions of mechanical treatment are the least studied. In the present paper we have tried to present the nature of the structural changes and to explain the essence of their influence on the dissolution of the activated phosphorites.

### EXPERIMENTAL

Syrian phosphorite with the following chemical composition 29.5%  $P_2O_5^{total}$ ; 6.9%  $P_2O_5^{cit. diss.}$ ; 3.2% F; 46.5% CaO; 0.55%  $R_2O_3$ ; (R=Al, Fe); 1.1%  $SO_3$ ; 7.3%  $SiO_2$ ; 0.35% MgO; 0.05% Cl; 6.2%  $CO_2$  was used for the purpose of this research;

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its moisture content is 3.14% and its mean granulometric particle composition 0.08 mm.

The mechanical activation of Syrian phosphorite was carried out by means of planet mill Pulverisette-5, Fritsch company (Germany) at a rotating speed of 320 min<sup>-1</sup>, activation time from 30 to 300 min; type of milling material – chrome nickel steel, weight of the milling material – 685 g; number – 22; diameter of the milling material – 20 mm. The mass of the samples for mechanical activation was 20 g.

The degree of transition from unassimilated into assimilated forms of phosphorus of Syrian phosphorite samples was assessed according to the content of soluble P<sub>2</sub>O<sub>5</sub> in 2% citric acid and ammonium citrate (pH=7), according to the Bulgarian standard 13418-80.

X-ray phase analyses were carried out by means of diffractometer DRON, radiation CuK<sub>α</sub>.

According to the data from the X-ray phase analysis the values of the amorphous level of the phosphorite were calculated using the following formula:  $A_m = 100 - K$ ,  $K = I_{ma} / I_{initial} \times 100$ , where  $K$  is the rate of change in the content of the crystal phase;  $I_{ma}$  and  $I_{initial}$  – the intensity of the main reflexes of the mechanically activated initial sample. The structure of the initial sample is accepted to be totally crystalline, not having an amorphous phase. The apatite amorphisation was calculated as a mean arithmetic sum from the intensity of the three reflexes with interplane distances:  $d = 2.78 \text{ \AA}$ ;  $2.69 \text{ \AA}$ ;  $2.62 \text{ \AA}$ .

The thermal analysis was carried out with a thermal complex 'Stanton Redcroft' (England), at a sample weight of  $15.20 \pm 0.4 \text{ mg}$ , in a temperature interval 288-1373 K, with a heat up speed of 10 K min<sup>-1</sup>.

## RESULTS AND DISCUSSION

The results from the chemical analysis of the 165 min activated phosphorites (Fig.1) register an increase in the dissolution in citric acid and ammonium cit-

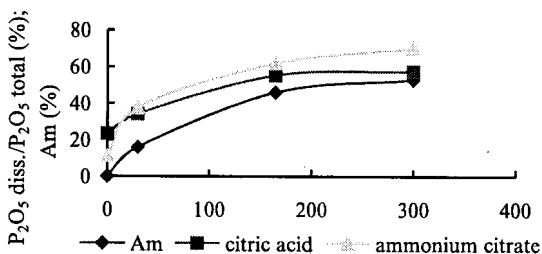
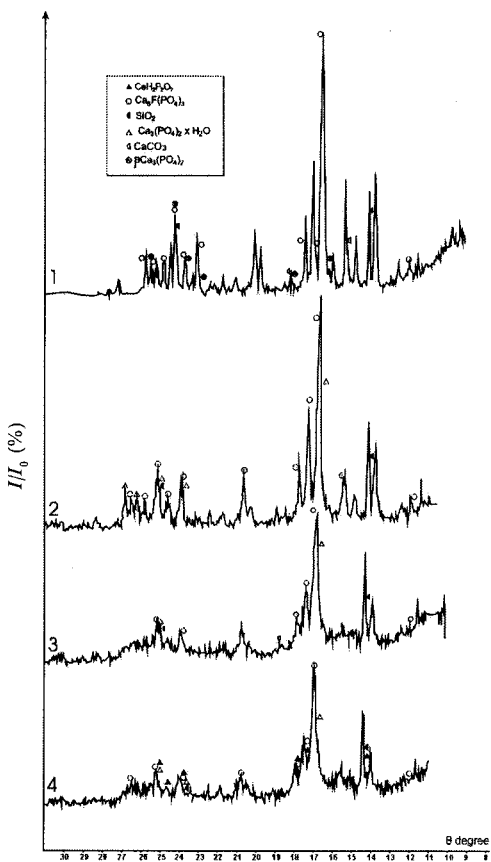


Fig. 1. Influence of the duration of mechanochemical effect on the dissolution of Syrian phosphorite in citric acid and ammonium citrate

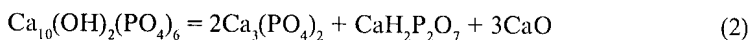
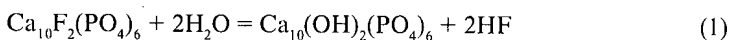
rate and the level of amorphism. The dissolution in citric acid reaches its maximum value at 165 min mechanical activation and then permanent value has been registered, which is the difference with the dissolution in ammonium citrate and which continuously increases and reaches up to 70% degree of transition from unassimilated into assimilated forms of phosphorus at a mechanical activation time 300 min. The dissolution increase of the activated phosphates is probably mainly due to the structural changes occurring in the initial phosphorite. The increased level of amorphism, which it bears is a proof for this assumption and there is an obvious tendency towards increase even after 165 min of mechanical activation. With the 300 min activated samples the amorphous level reaches 53%.

The diffractograms shown in Fig. 2 register a typical for the process of activation changes decrease in number and intensity of peaks at a strong widening of the basis, particularly well expressed with the main triplet of calcium



**Fig. 2.** Radiograms of Syrian phosphorites samples  
 1 – inactivated, 2– activated 30 min; 3 – activated 165 min, 4 – activated 300 min in a planet mill

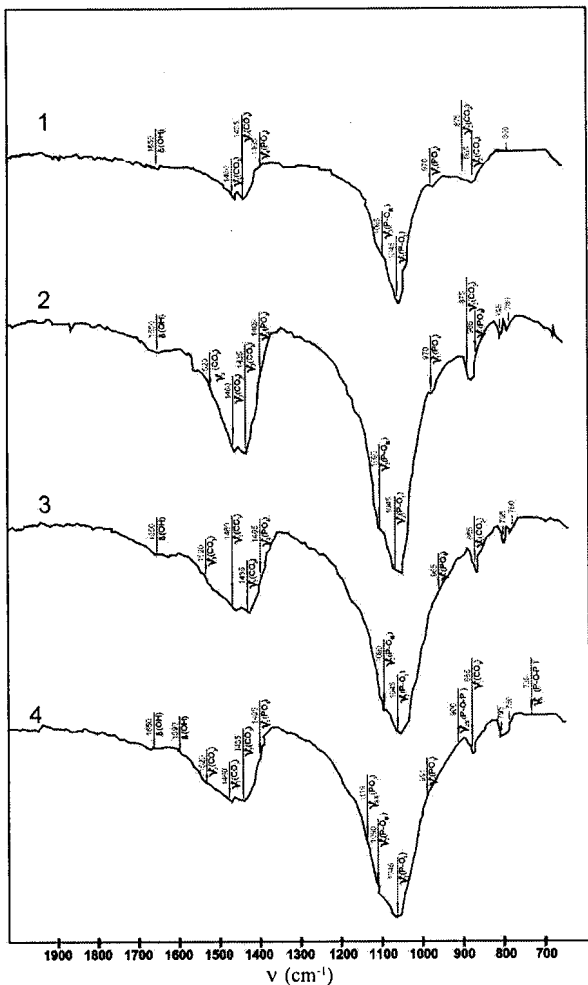
fluorineapatite (2.78 Å; 2.69 Å; 2.62 Å). Except for these structural changes, the X-ray structural data confirm the presence of diffraction lines of two new phases:  $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$  and  $\text{CaH}_2\text{P}_2\text{O}_7$ . The presence of these two new compounds in the solid product, after triboactivation is a proof for a hard-phase synthesis carried out for the activation period, which is probably accomplished after reactions (1)-(2).



We can assume that the increased dissolution of the activated after 165 min samples in ammonium citrate is due partly to the synthesised in the mechanical activation  $\text{CaH}_2\text{P}_2\text{O}_7$ .

In the radiogram of the initial phosphorite the admixture of  $\text{CaCO}_3$  is present as calcite with strongest expressed intensities at  $d=3.03$  Å; 3.86 Å; 2.49 Å. Because of its soft structure, it is early milled and it also makes the diffraction lines amorphous in the process of activation. They almost totally disappear from the diffractograms of the activated samples. Probably in the progress of activation mechanolysis of a part of the free carbonates flows and this adds to the increased dissolution of the activated samples.

In the ultra-red spectra of the initial Syrian phosphorite the basic lines of the valence variations of  $\text{PO}_4^{3-}$  ion are observed. According to the conditions of activation some of the bands are less intensive and others disappear. At more intensive treatment (sample 3 and sample 4 from Fig. 3) substantial changes in the spectra are registered. The bands of the symmetric valence variation  $\nu_1=970$   $\text{cm}^{-1}$  of the  $\text{PO}_4^{3-}$  ion disappear. The bands of the asymmetric valence variation  $\nu_3=1090$   $\text{cm}^{-1}$  of the  $\text{PO}_4^{3-}$  ion have the tendency to disappear, too. The valence variation  $\nu_3$  is determined by the connection variation P-O<sub>III</sub> in  $\text{PO}_4^{3-}$  tetrahedron. For the deformations occurred in the band at 1090  $\text{cm}^{-1}$  it is assumed that the structural violations on the first place affect the coordination complex  $\text{CaO}_6\text{F}$ , which leads to a change in the symmetry of the  $\text{PO}_4^{3-}$  ion and, respectively, to increased dissolution of the activated phosphates. A change occurs in the band of the  $\text{CO}_3^{2-}$  ion at 1400-1480  $\text{cm}^{-1}$  towards a tendency of less intensity and a replacement to higher wave numbers (an appearance of the band  $\nu_3=1520$   $\text{cm}^{-1}$ ). This confirms some authors' research that the presence of carbonates in the phosphorites leads to a strong violation of their structure because of  $\text{CO}_3^{2-}$  inclusion on the vacant places of the phosphate tetrahedron and the channel structure<sup>6</sup>. The bands of the OH<sup>-</sup> group at  $\delta(\text{OH}) = 1650$   $\text{cm}^{-1}$  undergo some changes, too. For the samples activated to 165 min, an increase in the intensity of the bands is registered, after 165-min mechanical activation a strong deformation occurs and it is expressed in their widening and decrease in the intensity which is typical for the amorphous structures. In the ultra-red spectra of the samples



**Fig. 3.** Ultra-red spectra of Syrian phosphates samples subjected to mechanochemical activation in a planet mill:

1 – inactivated; 2 – activated 30 min; 3 – activated 165 min, 4 – activated 300 min

activated for 300 min, an absorption band  $\delta(\text{H}) = 1590 \text{ cm}^{-1}$  appears which is probably due to the synthesised under mechanical activation  $\text{CaH}_2\text{P}_2\text{O}_7$ . This confirms the results from the X-ray phase analysis.

The derivatographic research of the inactivated and mechanically activated phosphates (Figs 4-7) confirm the conclusions from the chemical and spectroscopic analyses and give us additional information for the essence of the tribochemical activation. In the temperature interval 306-850 K we register a 2.3% increase of mass loss in the samples activated 30 min compared with the initial phosphorite. These changes can be explained when developing of the crystalline structure containing free crystallised and structurally connected water in

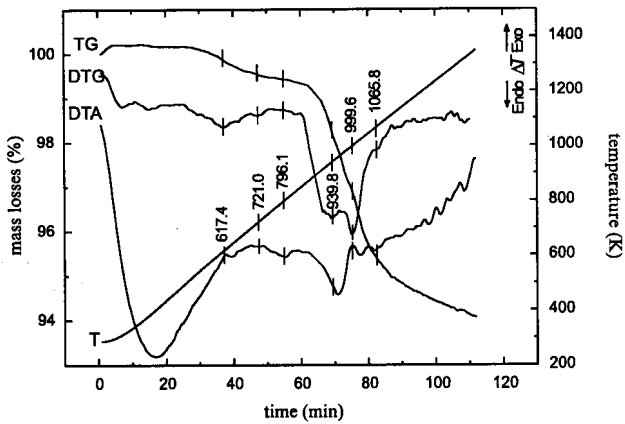


Fig. 4. TG-DTA analyses of inactivated Syrian phosphorite

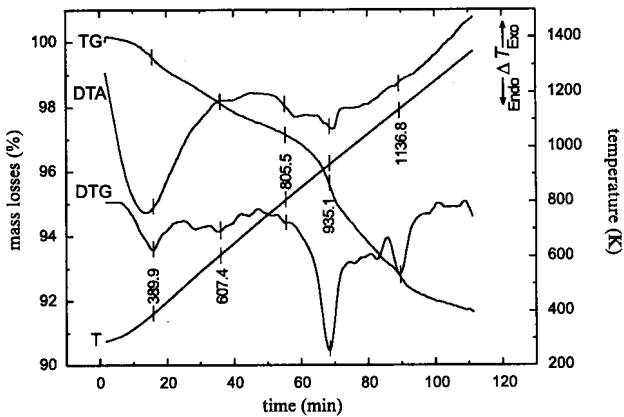


Fig. 5. TG-DTA dependencies of Syrian phosphorite 30 min activated in a planet mill

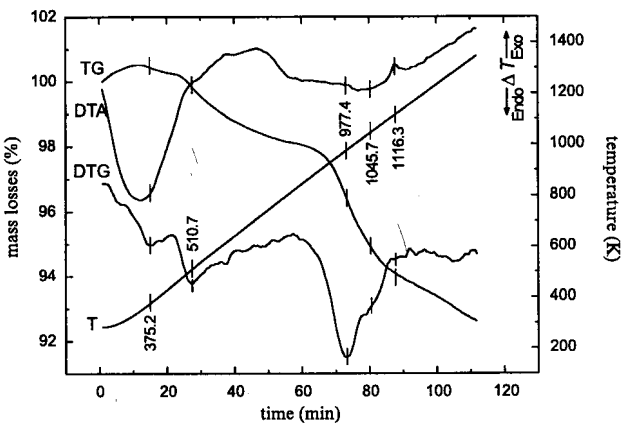


Fig. 6. TG-DTA dependencies of Syrian phosphorite 165 min activated in a planet mill

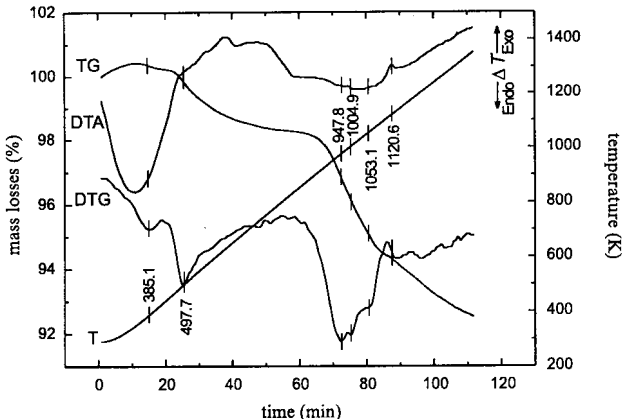
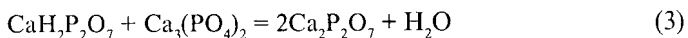


Fig. 7. TG-DTA dependencies of Syrian phosphorite 300 min activated in a planet mill

the mechanical activated process. Probably in this temperature interval dehydration of  $\text{Ca}_3(\text{PO}_4)_2 \cdot x\text{H}_2\text{O}$  is carried out. When the duration of the mechanical activation is increased, a decrease of mass loss is found out. It could be assumed that in the process of mechanical activation part of the free, connected by crystallisation water is transformed into structurally connected water following reactions (1) and (2), which confirms the results from the spectroscopic analyses. At the same time comparing the initial phosphorite with the activated samples a total decrease in their transition temperatures with approximately 300 K is registered. This proves the theory of intensifying the thermal decomposition processes of the triboactivated phosphates and the positive influence of the preliminary activation. The endothermic effects in the temperature interval 820-1015 K registered for the samples activated for 30 and 165 min are probably due to the precipitation of the structurally connected in the apatite structure  $\text{CO}_2$ . The increase in the mass loss in this temperature interval confirms the above stated assumption that when the duration of the mechanical activation is increased as a result of free carbonates mechanolysis a built-in of  $\text{CO}_2$  in the apatite structure is completed. This leads to considerable changes in the phosphate tetrahedron, which is in correlation with the increased dissolution of the activated phosphates. For the samples activated 300 min in the temperature interval 849-1031 K, an overlapping of the next two processes probably occurs – interaction of  $\text{CaH}_2\text{P}_2\text{O}_7$  with  $\text{Ca}_3(\text{PO}_4)_2$  following reaction (3) and a release of the built in the process of mechanical activation  $\text{CO}_2$ .



The endothermic effect in the next temperature interval 1045-1201 K registered is explained with the thermal decomposition of the free carbonates. In the temperature area 1116-1120 K for the samples activated for 165 and 300 min, an

exothermic effect missing in the thermal decomposition of the initial phosphorite is registered. The appearance of this exothermic effect is probably a consequence of the triboactivation under which influence the crystalline structure of the activated phosphates is deformed and mechanical energy is accumulated. This accumulated mechanical energy relaxes at 1116-1120 K and a spontaneous restructuring of the solid phase takes place. This confirms again the results from the spectroscopic analyses that as a result of the intensive mechanical activation applied a considerable structural changes occur in the initial phosphorite which is in correlation with the increased dissolution of the activated samples.

## CONCLUSIONS

The results from the chemical and spectroscopic analysis give us the reason to draw the following more important conclusions:

1. In the process of the mechanical activation a strong violation in the structure of the initial phosphorite occurs, i.e. a change in the symmetry of the crystalline lattice. It leads to a decrease and widening in some of the absorption bands of the fluorineapatite and probably an introduction of  $\text{CO}_3^{2-}$  groups in the phosphate tetrahedron and the channel structure.

2. As a result of the mechanical activation up to 300 min a partial mechanoanalysis of  $\text{Ca}_5\text{F}(\text{PO}_4)_3$  was proved in the presence of  $\text{H}_2\text{O}$  to  $\text{CaH}_2\text{P}_2\text{O}_7$ . Probably due to the  $\text{CaH}_2\text{P}_2\text{O}_7$  obtained under mechanochemical synthesis there is an increased dissolution of the 300-min activated samples.

In conclusion we can say that as a result of the structural changes in the initial phosphorite there is a considerable increase of its dissolution and under appropriate conditions of mechanical activation it could be used as phosphorous fertiliser with a high initial and continuous effect.

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