COMPARATIVE ANALYSIS OF THE MECHANOCHEMICAL HEM ACTIVATION EFFECT ON THE MICROSTRUCTURE AND PHASE TRANSFORMATIONS OF SEDIMENTARY APATITES

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ABSTRACT

High-energy-ball-milling (HEM) is a well-known approach for preparing various solid materials with increased reactivity. Such a manner of material activation is environmentally friendly and an alternative to the disadvantages of the traditional processing of phosphate raw materials that leads to pollution by solid phases and gaseous technological products.

This work investigates a natural CaO- P_2O_5 -SiO₂ system with 46.5 - 48.4 % CaO, 29.0 - 29.6 % P_2O_5 with a different amount of SiO₂ - from 1.9 to 7.3 %.

The samples were activated with 20 mm Cr/Ni bodies using a planetary ball mill for different times - 150 and 300 min. The structural, phase, and size transformations of the high-energy milled (HEM) samples in comparison to the raw samples were examined by chemical analysis low-temperature nitrogen adsorption (BET) method, powder X-ray diffraction (PXRD), and Fourier transform infrared (FT-IR) spectroscopy.

The obtained data indicate an increased defectiveness of the structure with prolonged HEM activation time leading to (i) the formation of XRD-amorphous particles, low-intensity and broadened peaks, (ii) increase of reactivity resulting in solid-phase crystallization of tri-calcium phosphates (TCP), pyro-phosphates (CPP), and (iii) isomorphic substitution of carbonate and hydroxyl ions for PO_4^{3-} and F^- with formation of carbonate-fluorine-hydroxyl-apatite, types A and AB.

Keywords: high-energy milling, reactivity, phosphate, quartz, isomorphic substitution.

INTRODUCTION

The natural mixture of apatite, quartz, and calcite is a well-known system (CaO-SiO₂-P₂O₅), investigated by many authors as a source of bone bioactive ceramic [1, 2], bioactive glass-polymer composites [3], ancient and modern cement [4 - 7], ceramic composites [8 - 12], phosphorus fertilizers, and soil improvers [13 - 16].

The main component of this natural mixture is the mineral apatite. In sedimentary deposits, the phosphorus content as P_2O_5 varies from 4 % to 20 %, and after enrichment - over 30%. Calcium's content in the form of CaO is about 45 - 48 %, silica is in the form of quartz with varying content [17, 18]. In phosphate ores and calcium-phosphate minerals, co-impurities such as quartz and calcite are important. Depending on the potential application of the natural CaO-SiO₂-P₂O₅ system, it can be processed using classical chemical methods with mineral acids [17, 19, 20], by thermal treatment, electrostatic separation, magnetic separation, chemical dissolution of carbonates, flotation and other approaches [21]. The minerals of the apatite group are characterized by low chemical activity and relatively high hardness (MSH = 5) according to the Mohs hardness scale (https://geology.com/minerals/mohshardness-scale.shtml). When choosing sustainable methods for the treatment of the apatite ore, the aim is to modify the properties of the apatite by increasing its reactivity and extracting the useful components. This needs to be achieved without extracting the heavy and radioactive chemical elements from the ore and releasing harmful gas emissions into the atmosphere. In addition, no solid-phase wastes should be generated, as these are the main problems with classical acid methods.

High-energy ball milling (HEM) is a well-known approach for preparing various solid materials and increasing their reactivity. This type of activation is a sustainable, ecological alternative to the disadvantages of the traditional processing of phosphate raw materials, which leads to pollution by solid phases and gaseous technological products [17, 22, 23].

The mechanochemical treatment of natural phosphates has a number of advantages: it allows the usage of crude phosphates that are ineffective for traditional technologies; it is friendly to the environment; the phosphorous fertilizers thus obtained are water insoluble; hence, they are not disposed of by groundwater in reservoirs. Due to these advantages, the method has great prospects for utilization in the fertilizer industry.

Our previous papers reported on the mechanochemical activation of North African phosphorites, where it was proven that an active phase with a lower degree of crystallinity and higher chemical activity is formed during the activation [22, 24]. The experiments were conducted while varying the activation parameters (grinding body type and activation time): plain steel (Fe) and alloy steel (Cr-Ni), and activation time up to 240 min with Cr-Ni steel and 300 min with plain steel. Powder X-ray and IR spectroscopic analyses revealed that during activation, the hydroxyl group is incorporated partially in the F-position while the CO₃²⁻ group is incorporated in the position of the phosphate ion, as well as into the vacancies of Ca2+ in the apatite structure. The isomorphic substitutions are evidenced by the formation of a carbonate-hydroxyl-fluorine-apatite in the activated samples. It has the general formula Ca₁₀(PO₄)₅CO₃(OH)F (COHFAp).

The formation of carbonate-fluorine-apatite of A-type because of the migration of carbonate ions from B-type to A-type and of CO_2 caught from the air, as well as of the residual calcite, are other proofs of the substitution [24]. Syrian and Tunisian phosphorites differ in their quartz content. Syrian phosphorites are comprised of greater amounts of the latter, which is a determining factor for the efficiency of mechanochemical activation.

The aim of this work is to investigate the structural changes resulting from the application of high energy milling (HEM) activation for a period of 150 and 300 min in a planetary ball mill by comparing the mechanochemical effect in sedimentary apatites originating from Tunisia and Syria depending on the same HEM conditions and the influence of the impurity composition. The achieved mechanochemical effect was evaluated using chemical analysis to determine the solubility of P_2O_5 in 2 % citric acid, the specific surface area (SSA) measurements by low-temperature nitrogen adsorption (BET) method, powder X-ray diffraction (PXRD), and Fourier transform infrared (FT-IR) spectroscopy.

EXPERIMENTAL

Materials

In the present work, natural CaO-SiO₂-P₂O₅ samples originating from Tunisia and Syria were investigated. The data about the chemical composition of Tunisian and Syrian apatites were presented in Table 1. Natural systems with a $P_2O_5^{total}$ % content above 10 % are commonly referred to as phosphorites [21]. By origin, Tunisian (Sample T) and Syrian (Sample S) phosphorites belong to the phosphate minerals resulting from sea water sedimentation. Phosphate ores are complex systems as far as their mineral composition and apatite structure are concerned, which has a propensity to cation and anion isomorphism. According to the structural chemical classification of M. V. Chaikina [17], Tunisian phosphorite (alkaline phosphorite group I) and Syrian phosphorite (alkaline phosphorite group II) belong to the "basic" apatites having a $(Ca/P)_{at} = 1.70 - 1.77$ ratio. Such apatites are formed in phosphate-calcium systems at pH> 7 and are characterized by enhanced defectiveness and isomorphic substitutions in the anion sub-lattice, mainly with carbonate ions. Considering the conditions under which they have been obtained, the basic minerals in Tunisian and Syrian phosphorites are apatite and calcite. The type of apatite is a carbonate-fluorine-apatite (C-F-Ap) B-type, where the compensation of the deficiency of PO₄³⁻ - ions is carried out by substitution with CO₃²⁻ μ F⁻ - a display of anionic isomorphism.

Methods

The initial sample of the Tunisian apatite is named T0 and that of the Syrian apatite - S0. The activated samples in the series with milling times: 10, 30, 60, 150, and 300 min were named T10, T30, T60, T150, and T300 and S10, S30, S60, S150, and S300, respectively.

The HEM activation was carried out in a planetary mill Pulverisette-5, Fritsch Company (Germany) at a rotating speed of 320 min⁻¹, activation time from 10 min to 300 min, Cr-Ni milling bodies with the following weight: 450 g; diameter of the milling bodies: 20 mm, sample mass: 20 g.

To evaluate the transition degree of the unassimilated forms of P_2O_5 in assimilated as a result of the HEM activation, a standard chemical method has been used for characterizing the dissolution of the phosphorous fertilizers in 2 % citric acid. The standardized methods for the determination of $P_2O_5^{ass}$ are the following:

- Bulgarian National Standard 14131-88, according to which $P_2O_5^{ass.}$ can be determined by direct extraction by 2 % citric acid;

- Instruction of EEO 77/535 p. 3.1.4 "Extraction of phosphorus soluble in neutral ammonium citrate" where the extraction of $P_2O_5^{ass}$ is performed by direct extraction.

The SSA measurements were performed by the BET-method (adsorptive gas N_2 , carrier gas He, heating temperature 150°C) using sorptometer EMS-53 and KELVIN 1040/1042 software (Costech International).

The experimental data for SSA and $P_2O_5^{ass}/P_2O_5^{tot}$ for all samples was mathematically processed to achieve the

best R fit (as close to 1 as possible) with a given function.

The powder X-ray diffraction (PXRD) measurements were made by D2 Phaser BrukerAXS, CuK α radiation ($\lambda = 0.15418$ nm) (operating at 30 kV, 10 mA) from 5 to 80°20 with a step of 0.05° (grinded sample with weight - 1.0 ± 0.1 mg and particle sizes below 0.075 mm. The database PDF (Powder Diffraction File, ICDD, 2001) was used for the determination of the phases and minerals present in the samples [25].

The Fourier Transform Infra-Red (FT-IR) spectra were registered on Bruker Tensor 37 spectrometer in the range 400 - 4000 cm⁻¹, using KBr pellet technique. A resolution of 2 cm⁻¹ was used collecting 60 scans for each sample.

For the present study to determine the chemical activity and specific surface area, the results of the examination of the complete series of HEM-activated samples of the two types of sedimentary apatites from Syria and Tunisia were analysed. To determine the structure-phase characteristics and evaluate the achieved mechanochemical effect and the influence of calcite and quartz impurities, the results of powder X-ray phase analysis and infrared spectroscopy of only the samples with the high activation times of 150 and 300 min were compared.

RESULTS AND DISCUSSION

Chemical analysis

The results from the chemical analysis of Tunisian and Syrian activated samples, which was carried out to define the content of $P_2O_5^{ass.}$ in a 2 % solution of citric acid with pH = 7, are presented in Fig. 1 as $P_2O_5^{ass/}P_2O_5^{tot}$ in %. With the increase in the duration of the HEM activation, the chemical analysis registers a high increase in the solubility in a 2 % solution of citric acid. The chemical analysis results of P_2O_5 solubility present a trend of rapid increase up to 150 min HEM,

Table 1. Chemical composition of the major ions comprising Tunisian and Syrian apatites and the present impurities, mass %.

Sample	$\begin{array}{c} P_2O_5^{\ total} \\ 90{0} \end{array}$	CaO %	SO _x %	SiO ₂ %	CO ₂ %	Cl ₂ %	R ₂ O ₃ * %	Na ₂ O %	K ₂ O %	MgO %	F ₂ %
Tunisian	29.58	48.40	3.58	1.88	6.48	0.017	1.07	1.38	0.07	0.67	2.74
Syrian	29.50	46.50	1.10	7.30	6.20	0.05	0.55	1.52	0.45	0.35	3.20

*(R = Al, Fe)

where 55.58 % is reached for the T series and 52.20 % for the S series. An increase is also found between 150 to 300 min, but at a much lower rate. After 300 min, an activation of 57.5 % is reached for the activated samples of Syrian phosphorite and 60.48 % for those, containing Tunisian phosphorite, in a 2 % solution of citric acid. The solubility of the phosphates in a 2 % solution of citric acid is accepted as an evaluation of the degree of deformation of the apatite structure, respectively, as an evaluation of the transition of the phosphorus in the soil solutions and the possibility for its absorption by plants. The important increase in the solubility of the activated sample in a 2 % solution of citric acid gives us reason to assume that in the process of activation there are substantial structural changes that lead to an increase in the content of $P_2O_5^{ass.}$.

Fig. 1 presents the exponential dependencies of $P_2O_5^{ass}$ % of HEM activation time for all samples. The solid lines present experimentally measured values, while the short-dotted lines - their best fits: $y = -27.76^* \exp(-x/72.00) + 60.04$ ($R^2 = 0.976$, sample T) and $y = -32.81^*\exp(-x/129.79) + 57.84$ ($R^2 = 0.996$, simple S). The exponential growth constants display the most rapid increase in the $P_2O_5^{ass}$ % with increasing HEM activation time for sample T, which contains lower amounts of SiO₂.

Specific surface area (SSA) measurements

As a result of the treatment in the planetary mill, the SSA of the phosphorite concentrates (T and S samples) increased during the first 10 - 30 min and decreased afterwards (Fig. 2). The decrease in SSA should be the result of the adhesion of the micro-particles [17, 26, 27]. The highest value of SSA achieved depends on the mineralogical composition and on the initial SSA of the sample. Two intervals were observed in both types of apatite: (i) a first interval of a sharp increase in SSA from 0 to 30 min HEM activation time, and (ii) a second interval with a decrease in SSA from 30 to 300 min HEM activation time. For the Tunisian phosphorite that contains the lowest amount of impurities, particularly quartz, and had the highest initial SSA, the SSA increased from 14.43 to 20.47 m² g⁻¹ in 10 min. For the Syrian phosphorite with low initial SSA - 9.95 m² g⁻¹ and high content of SiO_2 - 7.30 %, the highest value is 16.42 m² g⁻¹, respectively, and was obtained in 30 min. As it is shown in Fig. 2, the relative increase in SSA is

greater for the samples that contain less P_2O_5 and more impurity minerals, particularly silicates.

The data from the first interval were not used in the mathematical processing of the results due to the small number of points in them. The data from the second interval clearly show the decrease of values by exponential function for the samples from Tunisia and Syria in the following mathematical results: y = $17.67*\exp(-x/76.29) + 5.57$ (R² = 0.980, samples T0÷T300) and y = $17.25*\exp(-x/93.11) + 3.87$ (R2 = 0.981, simples S0÷S300). The SSA decreases more slowly for the sample with the higher quartz content, i.e. for the sample from Syria.

To confirm the data from the chemical analysis, some structural studies with physical methods as



Fig. 1. Functional dependencies of HEM activation time vs. $P_2O_5^{ass}/P_2O_5^{tot}$.



Fig. 2. Functional dependencies of HEM activation time vs. SSA.

X-ray phase analysis, structural analysis and infrared spectroscopy were carried out.

Powder XRD analysis

PXRD analysis was used to better evaluate and identify the phases present in the HEM activated samples at 150 min and 300 min. The obtained results for the raw material are shown in Fig. 3, 4 and Table 2.

For the changes occurring in the structure of the activated samples, respectively the degree of deformation of the crystal structure depending on the time of mechanical activation and the effect of HEM, conclusions were made from the changes in the PXRD diffractograms presented in (Figs. 3 and 4). When comparing the diffractograms of the unactivated phosphorites (T and S) with those of the activated ones, a trend towards a broadening of the peaks and a decrease in the intensity of the lines was found. This is particularly pronounced in the main triplet of calcium fluorapatite (2.78 Å; 2.69 Å; 2.62 Å) - insertion figures. The mixture of calcium fluorine-apatite (F-Ap), carbonate-hydroxyl-apatite (C-OH-Ap), carbonate-hydroxyl-fluorine-apatite (C-OH-F-Ap) and carbonate-apatite (C-Ap) in the activated samples established by XRD analysis indicates the isomorphic changes in the activated structure occurring during the treatment (Figs. 3 and 4, Table 2). They are



Fig. 3. XRD pattern of raw and HEM activated samples of Tunisian apatite.



Fig. 4. XRD pattern of raw and HEM activated samples of Syrian apatite.

assigned to the partial substitution of the phosphate group with a carbonate one and of the fluorine ion by a hydroxyl and/or carbonate one. Probably the isomorphic mixture thus obtained is not stoichiometric. Changes also occur in the mineral calcite. A part of it transforms into a metastable phase aragonite. In the diffractogram of a raw Syrian phosphorite, the impurity of CaCO₃ is present as calcite with the most pronounced intensities at d = 3.03 Å; 3.86 Å; 2.49 Å, which in the process of activation almost completely disappear from the diffractograms of the activated samples. This suggests that mechanical activation processes exert a strong mechanochemical effect on the free carbonates, which further contributes to enhancing the solubility of the activated samples.

The recorded changes in the diffractograms of the activated samples are evidence of the increased degree of amorphization and disruption of the three-dimensional periodicity of the structure characteristic of the crystalline state. In addition to these structural changes, the X-ray data demonstrate the presence of several new phases on the diffraction lines - β -Ca₃(PO₄)₂, β -Ca₂P₂O₇, b-Ca(PO₃)₂, Ca₂H₂P₂O₇ for the Tunisian HEM samples and CaSiO₃ for the Syrian HEM samples. The presence of these compounds in the post-triboactivation products is evidence of solid-phase synthesis occurring during the activation period. The presence of the structure.

No	Milling bodies	Time of HEM	Identify phases				
-	-	min	-				
1.	-	-	From initial samples				
			α SiO ₂ , Quartz (46-0145)	0.425, 0.334*, 0.182			
			CaCO ₃ , Calcite (47-1743)	0.303*, 0.193, 0.187			
			$Ca_5F(PO_4)_3$, (F-Ap) (15-0876)	0.279*; 0.270; 0.262			
			After HEM activation				
	Cr-Ni 20 mm		Isomorphic phases				
			Ca ₅ (PO ₄) ₃ OH, (OH-Ap) (09-0432)	0.281*, 0.277, 0.270			
			$Ca_{10}FOH(PO_{4})_{6}$, (F-OH-Ap)**	0.280*, 0.270, 0.261			
			$Ca_{10}(PO_4)_3(CO_3)_3(OH)_2,$				
2.			(C-OH-Ap) (19-0272)	0.346, 0.278*, 0.268			
			$Ca_{10}(PO_4)_5CO_3(OH)F$				
		10.200	(F-C-OH-Ap) (21-0145)	0.281, 0.271*, 0.226			
		10-300	New phases				
			CaH ₂ P ₂ O ₇ , (51-0200) (T only)	0.374, 0.335*, 0.318			
			β -Ca ₂ P ₂ O ₇ , (09-0346)	0.322, 0.309, 0.302*			
			β -Ca ₃ (PO ₄) ₂ , (09-0169)	0.321, 0.288*, 0.261			
			β-Ca(PO ₃) ₂ , (11-0039)	0.372, 0.351*, 0.313			
			CaSiO ₃ Wollastonite (42-0550),				
			(S only, after 300 min HEM)	$0.331, 0.309, 0.297^*$			

Table 2. X-ray phase analysis data for non-activated and HEM activated samples of Tunis and Syria.

* The strongest line; **F-OH-Ap [28]

FT-IR spectroscopy

The results from the infrared spectroscopic studies are presented in Figs. 5 - 8 and Table 3.

The deep structural deformations in the process of mechanical activation are evidenced by the IR results of the activated samples. In general, HEM activation mainly affects the main groups in the phosphorite structure - PO_4^{3-} ; $CO_3^{2-} \mu$ OH⁻ (Figs. 5 and 6). From the IR spectra of the activated phosphorites evidence is obtained for a typical mechanical activation broadening of the valence vibrational bands of PO₄³⁻ at 1045 cm⁻¹ towards the higher wavenumbers. The band at $n_1(PO_4^{3-}) =$ 970 cm⁻¹ decreases in intensity after 30 min of activation and tends to disappear. All this indicates a deformation of the close-range order. In the HEM process, the active surface area of the phosphorite increases in parallel with the uncovering of new surfaces, thereby accelerating the rate of binding with moisture from the air. This increase is well defined for the structurally bound OH⁻ ion ($n_2 = 1650 \text{ cm}^{-1}$). With the increase of the mechanical activation time, an increase in the intensities of absorption bands $n_2(CO_2) = 1435 \text{ cm}^{-1} \text{ M} n_2(CO_2) =$ 1460 cm⁻¹, is recorded, as well as the appearance of an additional band $n_2(CO_2) = 1520 \text{ cm}^{-1}$, which is assumed to be related to the incorporation of CO₃²⁻ into the sites with structural deformations of the activated phosphorite [28]. After 150 min of mechanical activation, a strong disruption of these bands occurs, expressed by their narrowing and decrease in intensity. The shift of the valence fluctuations of CO₃²⁻ to the higher wavenumbers confirms the studies and findings made by some authors [17] that the presence of carbonates in phosphorites leads to a strong deformation of their structure due to the incorporation of CO322 in the vacancies of the phosphate tetrahedron and channel structure, which may also explain the increased solubility of the activated samples in 2% citric acid. As the mechanical activation time increased to 150 min, the characteristic bands of the $P_2 O_7^{2-}$ ion $(n_{o}(P-O-P) = 725, 794 - 797 \text{ cm}^{-1}, n_{as}(PO_{3}) = 1095 - 1103$ cm^{-1} and $n_{as}(\text{PO}_3) = 1150 - 1178 \text{ cm}^{-1}$ also appeared in the IR spectra, confirming the XRD results [29].

The results obtained from the XRD and IR analyses prove the tendency of the phosphorus atom to form chains, which in this case occurs in the form of β -Ca₂P₂O₇ in the activated phosphorites. This is probably because of the accumulated mechanical energy and internal redistribution in the phosphorite structure, since the most energetically favourable group to form is that of $P_2O_7^{2^2}$.

For a more detailed analysis of the $v_3(CO_3)$ band of the carbonate ion, mathematical processing was performed for the decomposition of the band with a Gaussian function to determine the positions of the inserted bands. The data obtained proves the presence of



Fig. 5. IR of raw and HEM activated samples of Tunisian apatite.







Fig. 7. Decomposition of v_3 (CO₃) via Gauss function for T300.



Fig. 8. Decomposition of v_3 (CO₃) via Gauss function for S300.

additional inserted bands in the range 1500 - 1520 cm⁻¹, thus confirming the formation of A-type carbonate-apatite [30].

The broadening indicates the incorporation of the carbonate ions into the vacancies of the calcium ions in the apatite lattice, thus proving the formation of CFAp type A. Considering that it is non-stoichiometric, the compound can be represented by the general formula $Ca_{10-x}(PO_4)_{6-x}(F)_x(OH)_{2-x-2y}(CO_3)_y$, with $0 \le x \le 1.1$ and $0 \le y \le 0.2$ [30]. This confirms in particular the results from the XRD analysis.

The analysis of the results obtained from the chemical, X-ray and FT-IR-spectroscopic studies on activated samples of Tunisian and Syrian phosphorites allows for the assumption that mechanochemical treatment causes structural and phase changes in the apatite. The results of the chemical analysis demonstrate an increase in the amount of P_2O_5 in an assimilable form, while the specific surface data demonstrate an increase up to 30 min of activation with a subsequent decrease even below the levels of the initial values. A comparison of the two series demonstrates that the

solubility of the activated Tunisian apatite samples is higher than that of the Syrian samples. The results can be explained on one hand by an increase in the defectiveness of the apatite structure and on the other hand by the influence of the impurity minerals of calcite and quartz. The defectiveness of the structure is associated with a change in the structural parameters and energy accumulation resulting in the formation of a metastable solid phase with increased reactivity. It occurs precisely in the conversion of water-soluble and insoluble forms of P_2O_5 into assimilable ones and determines a potential application of activated apatites as fertilizers or improvers. Regarding the impurity minerals, it is suggested that quartz hinders the accumulation of mechanochemical energy in the Syrian samples and this is manifested in a lower rate of transformation of P_2O_5 into an assimilable form, hence solubility is lower (Fig. 1). Accordingly, quartz influences the specific surface (Fig. 2) by enhancing the interparticle agglomeration, resulting in lower values for Syrian apatite. Both effects of quartz are related to its higher hardness (Mohs scale = 7), so it influences the solubility by reducing it, while enhancing the agglomeration effect in the specific surface area. Calcite is a soft mineral (Mohs scale = 3), so its influence is not directly related to the solubility and specific surface area. HEM activation affects not only apatite, but also calcite and quartz. For quartz, the effect is minimal and is associated with a decrease in particle size (Figs. 3 and 4), whereas for calcite it is associated with an increase in chemical activity and participation in solid-phase synthesis reactions.

The structural changes lead to the formation of isomorphically substituted (at various degrees) hydroxyl carbonate fluorine apatites. The phase transformations are connected to the occurrence of solid-phase synthesis. It is identified by phases found in X-ray and IR spectroscopic analyses - Aragonite, C-OH-F-Ap, β -Ca(PO₃)₂, (X-ray and IR), A type C-Ap (IR), CaH₂P₂O₇ (IR).

The chemism of the isomorphic substitutions and the new phases resulting from the solid-phase synthesis could be presented by the following possible reactions (participated by water vapours and CO_2 from the air):

$$Ca_{10}(PO_4)_6F_2 = 3Ca_3(PO_4)_2 + CaF_2$$
 (1)

$$Ca_{10}(PO_4)_6F_2 + 2H_2O = Ca_{10}(PO_4)_6(OH)_2 + 2HF$$
 (2)

$$Ca_{10}(PO4)_{6}F_{2} + H_{2}O = Ca_{10}(PO_{4})_{6}(OH)F + HF$$
(3)
$$Ca_{10}(PO_{4})_{6}F_{2} + H_{2}O + CO_{2} + 2CaCO_{3} =$$

$$= Ca_{10}(PO_4)_4(CO_3)_3(OH)_2 + Ca(PO_3)_2 + CaF_2$$
(4)

$Ca_{10}(PO_4)_6F_2 + H_2O + 2CO_2 + CaCO_3 =$	
$= Ca_{10}(PO_4)_4(CO_3)_3OHF + Ca(PO_3)_2 + HF$	(5)
$Ca_{10}(PO_4)_6F_2 + H_2O = CaH_2P_2O_7 + 2Ca_3(PO_4)_2 + $	
$+ CaF_2 + 2CaO$	(6)
and/or	
$Ca_{10}F(OH)(PO_4)_6 + H_2O = CaH_2P_2O_7 + 2Ca_3(PO_4)_2$	+
+ 3CaO + HF	(7)
$CaH_2P_2O_7 + CaO = Ca_2P_2O_7 + H_2O$	(8)
$CaCO_3 + SiO_2 = CaSiO_3 + CO_2$	(9)
or	
$CaO + SiO_2 = CaSiO_3$	(10)

CONCLUSIONS

The results from the chemical, X-ray phase and FT-IR analyses of Tunisian and Syrian phosphorites activated by Cr-Ni milling bodies (d = 20 mm) for the period of 150 and 300 min allow for the following conclusions to be made:

1. The results of the chemical analysis demonstrate an increase in the chemical reactivity of the activated samples from Tunisia and Syria, which consists in the transformation of the water-soluble and non-assimilable forms of P_2O_5 into assimilable ones, the increase being more than twofold - from 29.13 % to 60.48 % for $P_2O_5^{ass}/P_2O_5^{total}$, % for the Tunisian series, and from 24.50 % to 57.50 % - for the Syrian series. The change in the specific surface area goes through a maximum (20.47 m² g⁻¹ for T10 and 16.42 m² g⁻¹ for S30) with a subsequent decrease as a result of agglomeration processes.

2. The results from the X-ray phase and FT-IR analyses of the natural Tunisian and Syrian phosphorites reveal the existence of a carbonate group substituting the phosphate one in the apatite structure - type B. Upon performing HEM activation, the formation of A-type carbonate-apatite was detected. The occurrence of solid-phase reactions with the formation of calcium silicates and calcium pyro- and metaphosphates under the influence of HEM conditions and the impurity minerals calcite and quartz are also proven.

3. X-ray phase and FT-IR analyses of the activated samples of Tunisian and Syrian phosphorites point at intensive isomorphic substitutions in the apatite structure at the F⁻ position along the hexagonal axis. Thus, the local loss of stability is greater and favours the formation of a metastable phase of enhanced chemical activity. These changes are more pronounced than those in the samples of the activated Syrian phosphorite and might be due to the differences in the nature of the two initial samples.

4. The results from the comparative analysis on the HEM activation effect indicate that under the same conditions, the Tunisian apatite responds better to the activation. This is due to the lower content of impurity minerals, especially quartz, and the use of the most efficient milling bodies of alloy Cr-Ni steel.

Funding

This work was supported by Contract №BG-RRP-2.004-0002-C01, BiOrgaMCT, Procedure BG-RRP-2.004 "Establishing of a network of research higher education institutions in Bulgaria ", funded by BULGARIAN NATIONAL RECOVERY AND RESILIENCE PLAN (E.S.)

Acknowledgements

The authors gratefully acknowledge to the Bilateral project between Tallinn University of Technology of Estonian Academy Sciences and "I. Kostov" Institute of Mineralogy and Crystallography of Bulgarian Academy of Sciences (2024 - 2025) (V.P., K.M., E.S.).

Authors' contributions: V.P.: conceptualization; E.S. and K.M.: sample preparation; V.P. and K.M.: PXRD and SEM analysis; V.P.: FT-IR analysis; V.P., V.S. and T.K.: writing original draft preparation; K.M. and T.K.: writing review and editing; E.S.: funding acquicition. All authors have read and aproved the final version of the manuscript.

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