

## Structural changes in the system natural apatite – NH<sub>4</sub> clinoptilolite during triboactivation

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The tribochemical activation of natural phosphate-clinoptilolite mixtures facilitates the transitions of hardly assimilated by plants P<sub>2</sub>O<sub>5</sub> forms into readily assimilated ones. Thus this approach is a solution of ecological and stuff problems, aiming to increase the transition of P<sub>2</sub>O<sub>5</sub> into assimilated by plants form. Mixtures of Tunisian phosphorite and NH<sub>4</sub>-exchanged clinoptilolite from Beli plast deposit (Bulgaria) (in different ratio) were activated in a planetary mill.

Structural changes in the mixtures during activation result in increasing of P<sub>2</sub>O<sub>5</sub> solubility. These changes were studied by XRD and IR spectroscopy. The obtained results show ion-exchange reactions between natural apatite and NH<sub>4</sub>-clinoptilolite and deformation or rupture of Si-O-Si and Si-O-Al bonds in the clinoptilolite structure on one hand, and defectiveness and isomorphism in the apatite structure on the other.

**Key words:** Apatite, NH<sub>4</sub>-clinoptilolite, tribochemical activation, XRD, IR spectroscopy.

### INTRODUCTION

Production of phosphorus fertilizers from natural apatite through conventional acid-treatment technologies leads to environmental problems, such as contamination with solid and gaseous waste. This is the reason to look for new non-conventional methods for obtaining of useful products from low-quality raw materials [1]. The assimilation degree of phosphorus fertilizers by plants is determined by the solubility of their main useful component – P<sub>2</sub>O<sub>5</sub>.

Natural zeolites improve the soil texture and increase the soil fertility due to their high ion-exchange capacity. Because of the alkali reaction of suspended zeolite they improve acidic soil and adsorb selectively heavy metals and radioactive isotopes. These factors determine the use of zeolite in a system with natural phosphates [2]. A controlled and renewable release fertilization system has been proposed, that employs NH<sub>4</sub> exchanged clinoptilolite to aid in dissolution of apatite and thereby in release of soluble N, P, and exchangeable Ca for uptake by plants [3].

The tribochemical activation (TCA) of natural phosphate-clinoptilolite mixtures is an alternative

solution of ecological and stuff problems, aiming to increase the transition of P<sub>2</sub>O<sub>5</sub> into assimilated by plants form (P<sub>2</sub>O<sub>5</sub><sup>ass</sup>). The applicability of TCA on phosphate and clinoptilolite minerals, their reactivity and interaction [4–6], thermal behaviour and solid phase reactions [7] have been studied.

The application of infrared spectroscopy and X-ray diffraction analysis allows the study of structural and phase transformations in the system apatite (Ap) – NH<sub>4</sub>-exchanged clinoptilolite (NH<sub>4</sub>-Cpt), with a focus on the changes that occur during TCA.

The aim of this study is to clarify how the structural changes during TCA and ion-exchange reactions in the system Ap–NH<sub>4</sub>-Cpt affect the solubility of P<sub>2</sub>O<sub>5</sub>.

### EXPERIMENTAL

Natural Cpt from Beli Plast deposit, Bulgaria and natural Ap from a Tunisian deposit were used in this work [6, 7, 8].

The clinoptilolite tuff contains about 80% clinoptilolite and impurities of montmorillonite, biotite, seledonite, low-crystobalite, quartz and feldspars. The chemical composition of isolated clinoptilolite (wt. %) is: SiO<sub>2</sub> – 66.15; Al<sub>2</sub>O<sub>3</sub> – 11.31; Fe<sub>2</sub>O<sub>3</sub> – 0.67; MgO – 0.46; CaO – 4.20; Na<sub>2</sub>O – 0.34; K<sub>2</sub>O – 3.13; H<sub>2</sub>O – 13.92. The tuff sample was treated with 1M solution of

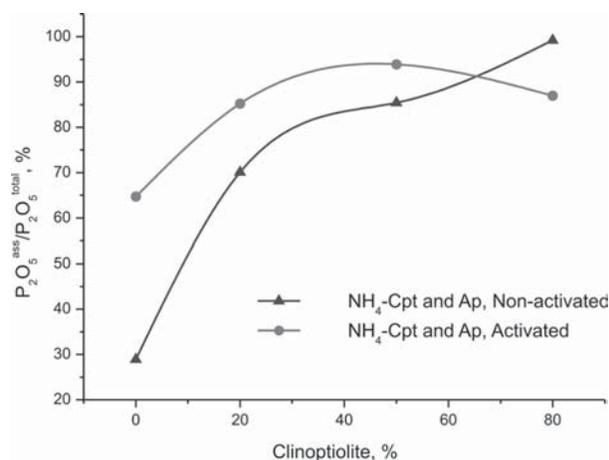
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NH<sub>4</sub>NO<sub>3</sub> by shaking for three days at 60 °C changing the solution every day and finally washed and dried at room temperature. The total cation exchange capacity with respect to Al content is 2.2 meq/g as the degree of ion exchange with NH<sub>4</sub><sup>+</sup> is higher than 98%. An evidence for NH<sub>4</sub><sup>+</sup> presence in the Cpt is the vibration doublet at 1446 and 1404 cm<sup>-1</sup> [7].

The natural Ap consists mainly of francolite (about 94%) and impurities of calcite, dolomite, feldspar, and quartz. The chemical composition of the Ap (wt. %) is: total P<sub>2</sub>O<sub>5</sub> – 29.00; R<sub>2</sub>O<sub>3</sub> – 1.07; SO<sub>3</sub> – 3.58, CaO – 48.40; MgO – 0.47; SiO<sub>2</sub> – 1.88; Na<sub>2</sub>O – 1.38; K<sub>2</sub>O – 0.07; F – 2.74; Cl – 0.056; CO<sub>2</sub> – 6.48. The initial Ap contains structural associated water and CO<sub>3</sub><sup>2-</sup> ions, substituting PO<sub>4</sub><sup>3-</sup> group (CO<sub>3</sub><sup>2-</sup> – B-type Ap). These data determine the used in this work sample as hydroxy-CO<sub>3</sub>-F-Ap [7].

Initial samples and three mixtures with different mass ratio of Ap to NH<sub>4</sub>-Cpt, namely 80:20, 50:50 and 20:80 were treated by tribochemical activation. The TCA was carried out in a planetary mill (Pulverisette-5, Fritsch Co, Germany) with agate milling bodies during 240 min and rotating speed of 280 min<sup>-1</sup>. Obtained samples were blended in 2% citric-acid solution since the variation of phosphate solubility was estimated by the phosphorus content in the solution. A standardized method for determination of P<sub>2</sub>O<sub>5</sub><sup>ass</sup> was used following Bulgarian National Standard 14131-88.

The X-ray diffraction (XRD) measurements of the samples were performed on D2 Phaser Bruker AXS, using a Ni-filtered Cu-K<sub>α</sub> radiation (λ = 0.15418 nm). A step-scan technique was applied with a step size of 0.05° 2θ and 3 s per step in the range 8–70° 2θ. Phase identification was performed using the index file PDF (Powder Diffraction File, ICDD, 2001).



**Fig. 1.** P<sub>2</sub>O<sub>5</sub><sup>ass</sup>/P<sub>2</sub>O<sub>5</sub><sup>total</sup> relations vs. clinoptilolite content in the mixtures

The Fourier transform infrared (FTIR) spectra were taken on a Bruker Tensor 37 spectrometer, using KBr pellet technique. A resolution of 2 cm<sup>-1</sup> was used collecting 120 scans for each sample.

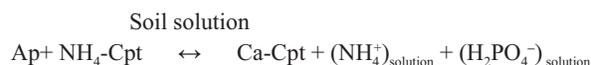
## RESULTS AND DISCUSSION

### Chemical results

Dependences of P<sub>2</sub>O<sub>5</sub><sup>ass</sup>/P<sub>2</sub>O<sub>5</sub><sup>total</sup> on NH<sub>4</sub>-clinoptilolite content in the mixture are presented on Fig. 1. The presented results show high degree of transition of P<sub>2</sub>O<sub>5</sub> into assimilated by plants form [7].

TCA improves the apatite reaction ability and solubility when the phosphate part dominates in the mixture.

The effect of ion-exchange reaction is manifested significantly when NH<sub>4</sub>-Cpt dominates in the non-activated system:



The combination of dissolution and ion-exchange reaction is more advantageous than applying each of the methods separately because both reactions drive each other [2, 3].

Chemical analyses give ground to suggest that some structural changes have occurred during the TCA in both components. The latter needs further evidences, provided by other structural methods.

### XRD data

XRD data of Ap and NH<sub>4</sub>-Cpt: initial samples (a) and activated (b) are presented on Fig. 2 while that of their mixtures on Fig. 3. The identified phases by XRD obtained during TCA are summarized in Table 1.

In the case of TCA, a tendency of amorphization for both samples and their mixtures is observed. Besides the expected decrease in intensity and widening of the peaks, peak splitting and appearance of new peaks are also recorded when Ap dominates in the mixture (Figs. 2 and 3a). Both reducing the intensity and peak widening are explained by crystallite size decrease. It has been shown [10, 11, 12], that under similar conditions of TCA of apatite samples, nano-sized particles of around 10-20 nm have been obtained. The result of the treatment is decreasing of the apatite structure stability and formation of nano-sized metastable phase with high chemical reactivity (Table 1). The appearance of new peaks in the main patterns of apatite (d = 2.79 Å) suggests the formation of new phase or the appearance of defects and isomorphous substitution.

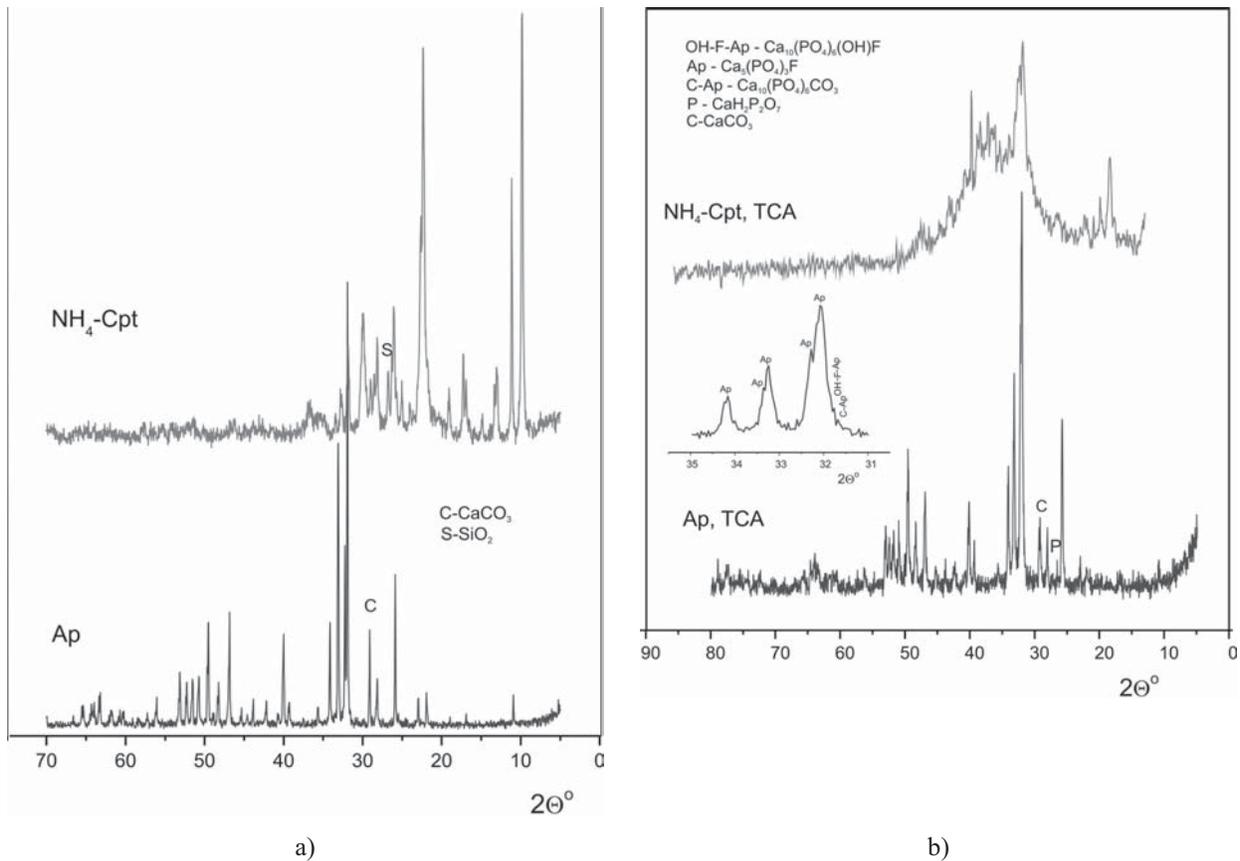


Fig 2. XRD data of initial (a) and tribo-activated (b) Ap and NH<sub>4</sub>-Cpt

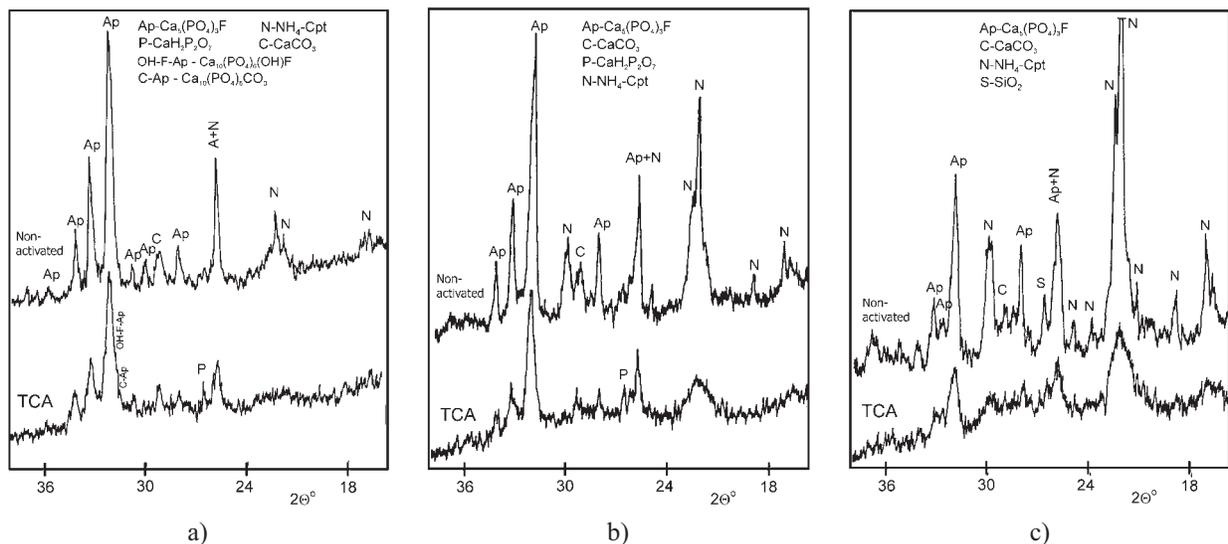


Fig. 3. XRD data of mixtures with Ap:NH<sub>4</sub>-Cpt ratio 80:20 (a); 50:50 (b); 20:80 (c)

The established phase composition suggests that the new peaks in Fig. 2b (small picture) should probably be attributed to the mixed type apatite: carbonate-apatite (C-Ap) and hydroxyl-carbonate

apatite-fluorine (C-OH-F-Ap). Their solid phase synthesis is associated with partial substitution of phosphate group by carbonate and fluorine ion by hydroxyl and/or carbonate. This substitution seems

**Table 1.** XRD data of Ap and NH<sub>4</sub>-Cpt and their mixtures

Sample	Identified phases
Nonactivated Ap	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> , CaCO <sub>3</sub>
Ap, TCA	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> , CaCO <sub>3</sub> , Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH)F [9], Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> CO <sub>3</sub> , CaH <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Ap+NH <sub>4</sub> -Cpt, 80:20, TCA	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> , CaCO <sub>3</sub> , Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> (OH)F [9], Ca <sub>10</sub> (PO <sub>4</sub> ) <sub>6</sub> CO <sub>3</sub> , CaH <sub>2</sub> P <sub>2</sub> O <sub>7</sub> , NH <sub>4</sub> -Cpt,
Ap+NH <sub>4</sub> -Cpt, 50:50, TCA	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> , CaCO <sub>3</sub> , NH <sub>4</sub> -Cpt, CaH <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Ap+NH <sub>4</sub> -Cpt, 20:80, TCA	Ca <sub>5</sub> F(PO <sub>4</sub> ) <sub>3</sub> , CaCO <sub>3</sub> , NH <sub>4</sub> -Cpt, SiO <sub>2</sub>
Nonactivated NH <sub>4</sub> -Cpt	NH <sub>4</sub> -Cpt, SiO <sub>2</sub>
NH <sub>4</sub> -Cpt, TCA	NH <sub>4</sub> -Cpt, SiO <sub>2</sub>

to be facilitated by local temperature increase, due to both impact and friction effects. The resulting isomorphous phase is probably non-stoichiometric.

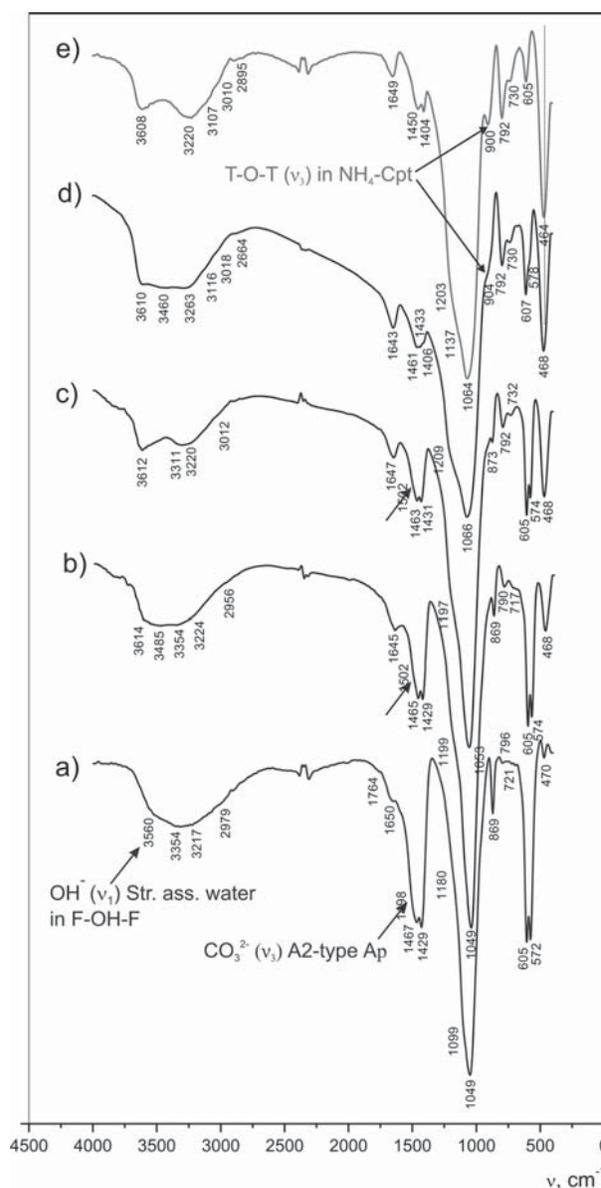
### IR spectra

IR spectra of TCA samples with different mixing ratio are presented on Fig. 4, while their band positions and types of fundamental vibrational modes are listed in Table 2.

*In the case of NH<sub>4</sub>-Cpt domination* (Figs. 4 and 5a) a new vibration band at 900 cm<sup>-1</sup> appears (ν<sub>3</sub>, asymmetric stretching mode T-O-T, T=Si, Al). This band misses in nonactivated samples, while in activated samples it is related to the processes of deformation and rupture of intertetrahedral bonds – Si-O-Si or Si-O-Al [5, 13]. According to the theory of tribochemical activation, as a result of deformation and rupture of individual bonds in Si-O-Al groups, active centres are formed in the zeolite structure, which then interact with the phosphate.

*In the case of Ap domination* (Figs. 4 and 5b and c): Spectra of Fig. 5b focus on changes in the positions of the carbonate ion in the activated samples. Under the influence of TCA, changes of absorption bands of carbonate group incorporated in the apatite structure occur (ν<sub>3</sub> = 1400–1470 cm<sup>-1</sup>). In studied samples an irregular widening of the left slope of the band are recorded, due to the appearance of a low-intensity band at about 1503 cm<sup>-1</sup>. A peak fitting procedure via Gaussian function was applied to determine this position. (Fig. 5b small picture). The presence of this bend is probably due to the incorporation of carbonate ions in the apatite structure during tribochemical activation, which is an evidence for the formation of Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>CO<sub>3</sub> and Ca<sub>10</sub>(PO<sub>4</sub>)<sub>5</sub>CO<sub>3</sub>(OH)F (Table 1).

Given the results of both XRD analysis and IR spectroscopy a conversion of inactive phosphate – Ca<sub>5</sub>(PO<sub>4</sub>)<sub>3</sub>F, type B into Ca<sub>10</sub>(PO<sub>4</sub>)<sub>5</sub>CO<sub>3</sub>(OH)F and Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>CO<sub>3</sub> is assumed, as the carbonate



**Fig. 4.** IR spectra of TCA samples: a) Ap; b) 80:20; c) 50:50; d) 20:80 and e) NH<sub>4</sub>-Cpt

**Table 2.** IR data of Ap and NH<sub>4</sub>-Cpt and their mixtures in mode of TCA

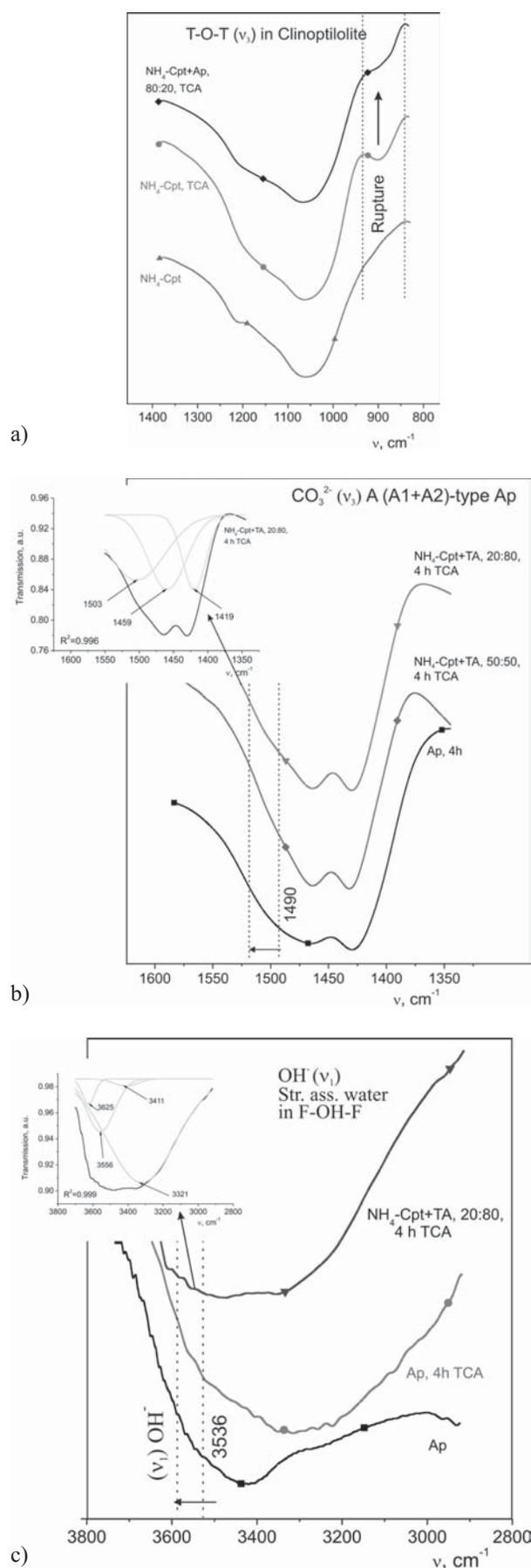
No	Band position, cm <sup>-1</sup>					Vibrational Mode
	Ap	20:80	50:50	80:20	NH <sub>4</sub> -Cpt	
1.	470	468	468	468	464	Symmetric O-P-O (ν <sub>2</sub> ) bending mode in C-F-Ap Symmetric T-O-T (T=Si, Al) (ν <sub>2</sub> ) bending mode in NH <sub>4</sub> -Cpt and Symmetric (ν <sub>1</sub> ) stretching mode Me-O (Me= Si, Al)
2.	572 605	574 605	574 605	578 607	– 605	Asymmetric O-P-O (ν <sub>4</sub> ) bending mode in B-type C-F-Ap Asymmetric O-T-O (T=Si, Al) (ν <sub>4</sub> ) bending mode in NH <sub>4</sub> -Cpt
3.	721	717	–	–	–	Asymmetric O-C-O (ν <sub>4</sub> ) bending mode of CO <sub>3</sub> <sup>2-</sup> in B-type C-F-Ap
4.		790	732 792	730 792	730 792	Symmetric (ν <sub>1</sub> ) stretching mode O-T-O (T= Si, Al) in NH <sub>4</sub> -Cpt [20]
5.	869	869	873	–	–	Symmetric O-C-O (ν <sub>2</sub> ) bending mode in CaCO <sub>3</sub> and B-type CO <sub>3</sub> <sup>2-</sup> in C-F-Ap
6.	–	–	–	904	900	Asymmetric T-O-T (T=Si, Al) (ν <sub>3</sub> ) stretching mode in NH <sub>4</sub> -Cpt [5]
7.	1049 1099 – 1180	1049 – – 1199	1053 – – 1197	1066 – – 1209	1064 – 1137 1203	Asymmetric P-O-P (ν <sub>3</sub> ) stretching mode of PO <sub>4</sub> <sup>3-</sup> in C-F-Ap
8.	–	–	–	1406	1404	Asymmetric N-H (ν <sub>4</sub> ) bending mode of NH <sub>4</sub> <sup>+</sup> in NH <sub>4</sub> -Cpt
9.	1429 – 1467	1429 – 1465	1431 – 1463	1433 – 1461	1450 –	Asymmetric C-O (ν <sub>3</sub> ) stretching mode of CO <sub>3</sub> <sup>2-</sup> in B-type CFAp and CaCO <sub>3</sub>
10.	1498	1502	1502	–	–	Asymmetric C-O (ν <sub>3</sub> ) stretching mode A2-type CO <sub>3</sub> <sup>2-</sup> in C-OH-F-Ap [1, 15]
11.	1650 1764	1645 –	1647 –	1643 –	1649 –	Symmetric OH <sup>-</sup> (ν <sub>2</sub> ) bending mode in zeolitic water
12.	–	–	3012	3018	3010	Symmetric N-H (ν <sub>1</sub> ) stretching mode of NH <sub>4</sub> <sup>+</sup> in NH <sub>4</sub> -Cpt
13.	–	–	–	3116	3107	Asymmetric N-H (ν <sub>3</sub> ) stretching mode of NH <sub>4</sub> <sup>+</sup> in NH <sub>4</sub> -Cpt
14.	3200– 3430	3230– 3485	3240– 3440	3220– 3440	3230– 3430	Symmetric OH <sup>-</sup> (ν <sub>1</sub> ) stretching mode in zeolitic water
15.	3560	–	–	–	–	Symmetric OH <sup>-</sup> (ν <sub>1</sub> ) stretching mode in structure associate water [21]
16.	–	3614	3612	3610	3608	Symmetric (ν <sub>1</sub> ) stretching mode of OH <sup>-</sup> directly bonded to Si [22]

ion occupies A (A2) type position [14–17]. Such carbonate ion substitutions in the apatite structure result in samples with violated stoichiometry (Ca/P > 1.667). This carbonate-containing, non-stoichiometric apatite is thermally less stable and exhibits higher citrate and citric solubility [7, 18].

Similar changes occur in the positions of the hydroxyl ion as a result of TCA (Fig. 5c). Both decrease of band intensity and appearance of new low intensity bands in the range 3535–3540 cm<sup>-1</sup>, indicating increased amount of OH<sup>-</sup> in fluorine chains

(F-OH-F) have been observed.(Fig. 5c small picture). This leads to a band shift [19] towards the higher frequency, illustrated by the spectra on Figs. 4–5c. Observed effects are in correlation with the concept of formation of nano-sized phase with low degree of crystallinity and increased solubility of the activated samples in 2% citric acid.

The XRD and IR spectroscopy data in this work are confirmed by results, concerning the thermal behaviour of TCA Tunisian apatite and its mixture with Cpt [7]. It has been considered that changes



**Fig. 5.** Structural changes observed in IR spectra of: a) samples with NH<sub>4</sub>-Cpt domination; b) and c) samples with Ap domination

in the temperature range 520–840 °C are related to isomorphous substitutions in the apatite structure.

## CONCLUSIONS

- The TCA leads to deformation and rupture of Si-O-Si and Si-O-Al bonds and decreasing of ion-exchange capacity in the clinoptilolite sample;
- The activation provokes amorphization and structural defects in apatite structure, which leads to increased reactivity, especially in the case of apatite domination;
- The results of the applied methods provide the opportunity to explore the structural and phase transformations, reactions of solid phase synthesis and degradation in natural samples and their mixtures, as well as to select the most appropriate conditions for tribochemical treatment.

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## СТРУКТУРНИ ПРОМЕНИ В СИСТЕМАТА ПРИРОДЕН АПАТИТ – NH<sub>4</sub> КЛИНОПТИЛОЛИТ ПРИ ТРИБОАКТИВАЦИЯ

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(Резюме)

Трибоактивацията на смеси от природен фосфат и клиноптилолит благоприятства преминаването на трудно усвояемите от растенията P<sub>2</sub>O<sub>5</sub> форми в лесноусвояеми. Това е един нетрадиционен метод за решаване на екологични и суровинни проблеми. Смеси от туниски фосфорит и NH<sub>4</sub>-обменена форма на клиноптилолит от българското находище Бели Пласт (в различно отношение) са активирани в планетарна мелница. Структурните промени в смесите, в резултат на активацията, рефлектират върху повишаване на разтворимостта на P<sub>2</sub>O<sub>5</sub>. Тези промени са констатирани с помощта на XRD метод и IR спектроскопия. Получените резултати показват протичането на йонообменни реакции между природния апатит и NH<sub>4</sub> клиноптилолит както и деформация или прекъсване на Si-O-Si и Si-O-Al връзки в клиноптилолита, от една страна и изоморфизъм в структурата на апатита от друга страна.