Structural changes in the system natural apatite – NH₄ clinoptilolite during triboactivation

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The tribochemical activation of natural phosphate-clinoptilolite mixtures facilitates the transitions of hardly assimilated by plants P₂O₅ forms into readily assimilated ones. Thus this approach is a solution of ecological and stuff problems, aiming to increase the transition of P₂O₅ into assimilated by plants form. Mixtures of Tunisian phosphorite and NH₄-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 P₂O₅ solubility. These changes were studied by XRD and IR spectroscopy. The obtained results show ion-exchange reactions between natural apatite and NH₄-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, NH₄-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 row materials [1]. The assimilation degree of phosphorus fertilizers by plants is determined by the solubility of their main useful component – P₂O₅.

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 NH₄ 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 P₂O₅ into assimilated by plants form (P₂O₅ass). 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) – NH₄-exchanged clinoptilolite (NH₄-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–NH₄-Cpt affect the solubility of P₂O₅.

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, seladonite, low-crystobalite, quartz and feldspars. The chemical composition of isolated clinoptilolite (wt. %) is: SiO₂ – 66.15; Al₂O₃ – 11.31; Fe₂O₃ – 0.67; MgO – 0.46; CaO – 4.20; Na₂O – 0.34; K₂O – 3.13; H₂O – 13.92. The tuff sample was treated with 1M solution of
NH₄NO₃ 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 NH₄⁺ is higher than 98%. An evidence for NH₄⁺ presence in the Cpt is the vibration doublet at 1446 and 1404 cm⁻¹ [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 P₂O₅ – 29.00; R₂O₃ – 1.07; SO₃ – 3.58; CaO – 48.40; MgO – 0.47; SiO₂ – 1.88; Na₂O – 1.38; K₂O – 0.07; F – 2.74; Cl – 0.056; CO₂ – 6.48. The initial Ap contains structural associated water and CO₃²⁻ ions, substituting PO₄³⁻ group (CO₃²⁻ – B-type Ap). These data determine the used in this work sample as hydroxy-CO₃²⁻-F-Ap [7].

Initial samples and three mixtures with different mass ratio of Ap to NH₄-clinoptilolite, 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⁻¹. 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 P₂O₅ ass was used following Bulgarian National Standard 14131-88.

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

RESULTS AND DISCUSSION

Chemical results

Dependences of P₂O₅ ass/P₂O₅ total on NH₄-clinoptilolite content in the mixture are presented on Fig. 1. The presented results show high degree of transition of P₂O₅ 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 NH₄-capt dominates in the non-activated system:

Soil solution
Ap + NH₄-Cpt ↔ Ca-Cpt + (NH₄)solution + (H₂PO₄⁻)solution

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 NH₄-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 the TCA in both components. The latter needs further evidences, provided by other structural methods.
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
to be facilitated by local temperature increase, due to both impact and friction effects. The resulting isomorphic 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 NH₄-Cpt domination (Figs. 4 and 5a) a new vibration band at 900 cm⁻¹ appears (ν₃, 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 (ν₃ = 1400–1470 cm⁻¹). 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⁻¹. 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 Ca₁₀(PO₄)₆CO₃ and Ca₁₀(PO₄)₅CO₃(OH)F (Table 1).

Given the results of both XRD analysis and IR spectroscopy a conversion of inactive phosphate – Ca₅(PO₄)F, type B into Ca₁₀(PO₄)₆CO₃(OH)F and Ca₁₀(PO₄)₆CO₃ is assumed, as the carbonate

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**Table 1. XRD data of Ap and NH₄-Cpt and their mixtures**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Identified phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nonactivated Ap</td>
<td>Ca₃F(PO₄)₆, CaCO₃</td>
</tr>
<tr>
<td>Ap, TCA</td>
<td>Ca₃F(PO₄)₆, CaCO₃, Ca₁₀(PO₄)₅(OH)F [9], Ca₁₀(PO₄)₅CO₃, CaH₂P₂O₇</td>
</tr>
<tr>
<td>Ap+NH₄-Cpt, 80:20, TCA</td>
<td>Ca₃F(PO₄)₆, CaCO₃, Ca₁₀(PO₄)₅(OH)F [9], Ca₁₀(PO₄)₅CO₃, CaH₂P₂O₇, NH₄-Cpt</td>
</tr>
<tr>
<td>Ap+NH₄-Cpt, 50:50, TCA</td>
<td>Ca₃F(PO₄)₆, CaCO₃, NH₄-Cpt, CaH₂P₂O₇</td>
</tr>
<tr>
<td>Ap+NH₄-Cpt, 20:80, TCA</td>
<td>Ca₃F(PO₄)₆, CaCO₃, NH₄-Cpt, SiO₂</td>
</tr>
<tr>
<td>Nonactivated NH₄-Cpt</td>
<td>NH₄-Cpt, SiO₂</td>
</tr>
<tr>
<td>NH₄-Cpt, TCA</td>
<td>NH₄-Cpt, SiO₂</td>
</tr>
</tbody>
</table>

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**Fig. 4. IR spectra of TCA samples: a) Ap; b) 80:20; c) 50:50; d) 20:80 and e) NH₄-Cpt**
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⁻¹, indicating increased amount of OH⁻ 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

<table>
<thead>
<tr>
<th>No.</th>
<th>Band position, cm⁻¹</th>
<th>Vibrational Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ap 20:80 50:50 80:20 NH₄-Cpt</td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>470 468 468 468 464</td>
<td>Symmetric O-P-O (v₂) bending mode in C-F-Ap</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Symmetric T-O-T (T-Si, Al) (v₂) bending mode in NH₄-Cpt and Symmetric (v₁) stretching mode Me-O (Me= Si, Al)</td>
</tr>
<tr>
<td>2.</td>
<td>572 574 574 578 605</td>
<td>Asymmetric O-P-O (v₄) bending mode in B-type C-F-Ap</td>
</tr>
<tr>
<td></td>
<td>605 605 607 607 605</td>
<td>Asymmetric O-T-O (T=Si, Al) (v₄) bending mode in NH₄-Cpt</td>
</tr>
<tr>
<td>3.</td>
<td>721 717 – – –</td>
<td>Asymmetric O-C-O (v₄) bending mode of CO₃²⁻ in B-type C-F-Ap</td>
</tr>
<tr>
<td>4.</td>
<td>790 732 730 792 792</td>
<td>Symmetric (v₁) stretching mode O-T-O (T=Si, Al) in NH₄-Cpt [20]</td>
</tr>
<tr>
<td>5.</td>
<td>869 869 873 – –</td>
<td>Symmetric O-C-O (v₄) bending mode in CaCO₃ and B-type CO₃²⁻ in C-F-Ap</td>
</tr>
<tr>
<td>6.</td>
<td>– – – 904 900</td>
<td>Asymmetric T-O-T (T=Si, Al) (v₅) stretching mode in NH₄-Cpt [5]</td>
</tr>
<tr>
<td>7.</td>
<td>1049 1049 1053 1066 1064</td>
<td>Asymmetric P-O-P (v₅) stretching mode of PO₄³⁻ in C-F-Ap</td>
</tr>
<tr>
<td></td>
<td>1099 – – – –</td>
<td>Asymmetric P-O-P (v₅) stretching mode of PO₄³⁻ in C-F-Ap</td>
</tr>
<tr>
<td></td>
<td>1180 1199 1197 1209 1203</td>
<td>Asymmetric P-O-P (v₅) stretching mode of PO₄³⁻ in C-F-Ap</td>
</tr>
<tr>
<td>8.</td>
<td>– – – 1406 1404</td>
<td>Asymmetric N-H (v₅) bending mode of NH₄⁺ in NH₄-Cpt</td>
</tr>
<tr>
<td>9.</td>
<td>1429 1429 1431 1433 1450</td>
<td>Asymmetric C-O (v₅) stretching mode of CO₃²⁻ in B-type C-F-Ap and CaCO₃</td>
</tr>
<tr>
<td>10.</td>
<td>1498 1502 1502 – –</td>
<td>Asymmetric C-O (v₅) stretching mode A₂-type CO₃²⁻ in C-OH-F-Ap [1, 15]</td>
</tr>
<tr>
<td>11.</td>
<td>1650 1764 1645 1647 1643 1649</td>
<td>Symmetric OH⁻ (v₅) bending mode in zeolitic water</td>
</tr>
<tr>
<td>12.</td>
<td>– – 3012 3018 3010</td>
<td>Symmetric N-H (v₅) stretching mode of NH₄⁺ in NH₄-Cpt</td>
</tr>
<tr>
<td>13.</td>
<td>– – 3116 3107</td>
<td>Asymmetric N-H (v₅) stretching mode of NH₄⁺ in NH₄-Cpt</td>
</tr>
<tr>
<td>15.</td>
<td>3560 – – – –</td>
<td>Symmetric OH⁻ (v₅) stretching mode in structure associate water [21]</td>
</tr>
<tr>
<td>16.</td>
<td>– 3614 3612 3610 3608</td>
<td>Symmetric (v₁) stretching mode of OH⁻ directly bonded to Si [22]</td>
</tr>
</tbody>
</table>
in the temperature range 520–840 °C are related to isomorphic 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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REFERENCES


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(Резюме)

Трибоактивацията на смеси от природен фосфат и клиноптилолит благоприятства преминаването на трудно усвояемите от растенията P₂O₅ форми в лесноусвояеми. Това е един нетрадиционен метод за решаване на екологични и суровинни проблеми. Смеси от туниски фосфорит и NH₄-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 P₂O₅. Тези промени са констатирани с помощта на XRD метод и IR спектроскопия. Получените резултати показват протичането на йонообменни реакции между природния апатит и NH₄ клиноптилолит както и деформация или прекъсване на Si-O-Si и Si-O-Al връзки в клиноптилолита, от една страна и изоморфизмът в структурата на апатита от друга страна.