Available online at www.sciencedirect.com

SCIENCE DIRECT®

Thermochimica Acta 404 (2003) 155–162

thermochimica acta

www.elsevier.com/locate/tca

Thermal treatment of mixtures of Tunisian phosphorite and additives of aluminum silicate

D. Bojinova

University of Chemical Technology and Metallurgy, 8 Kl. Ohridski blvd., 1756 Sofia, Bulgaria

Received 7 August 2002; received in revised form 10 February 2003; accepted 12 February 2003

Abstract

The process in the mixtures of Tunisian phosphorite (TP) with addition of aluminum silicate waste by chemical and X-ray diffraction (XRD) analyses was studied. The influence of the additive's quantity, the temperature of thermal treatment, as well as the mechanical activation on the solubility of the heated mixtures in various extracting agents (citric acid, ammonium citrate and formic acid), were investigated. The solubility of P_2O_5 is higher in the case of the calcined and mechanically activated TP and its mixtures with "Medet's steryl" (MS) compared to the non-activated TP and its mixtures. The activated mixtures with 20% of MS have highest rate of P_2O_5 solubilization in citrate acid (66%) as well into ammonium citrate soluble form (60%).

New phases [$Ca_5(PO_4)_3(OH)$, $Ca_5(PO_4)_2{\cdot}SiO_4$, $Ca_7(PO_4)_2{\cdot}(SiO_4)_2$ and $Ca_4P_2O_9$] in non-activated and activated calcined products were determined using XRD analysis.

© 2003 Elsevier Science B.V. All rights reserved.

Keywords: Thermophosphate fertilizers; Aluminum silicate; Fluorapatite; Mechanical activation; Thermal treatment

1. Introduction

The development of new non-acid methods for obtaining of slow active fertilizers is a modern tendency in the mineral fertilizer's technology. In this respect, a combination of thermal and mechano-chemical processing is very promising.

There are data in the literature concerning the combined thermal treatment of natural phosphates and Si-containing minerals [1–4].

The reactions in mixtures of hydroxylapatite and natural alumosilicate (nepheline, glauconite and pseudoleicite) or shungite during their thermal treatment (1100–1400 °C) for 1 h, the phase composition and the solubility of the calcined product in 2% citric acid solution were studied by chemical, IR and X-ray diffraction (XRD) analyses [1,2].

The influence of additives (SiO_2, MgO, Al_2O_3 and Fe_2O_3), as well as natural alumosilicates (nepheline, glauconite and pseudoleicite), on the citrate solubility of calcined mixtures at 1350–1400 °C for 90 min was investigated [3]. In the mixtures with nepheline and pseudoleicite and molar ratio of $SiO_2:P_2O_5 > 0.21$ and $CaO:P_2O_5 = 2.0–3.0$, the solubility of P_2O_5 was 97–98%. In the mixtures with glauconite the solubility of P_2O_5 was as much as 10% lower.

The solubility of P_2O_5 in mixtures of natural phosphates with 20% SiO_2 thermally treated at 1350, 1400 and 1450 °C in the presence of water vapor for 15, 30, 60 and 120 min was studied [4]. The results from the chemical and XRD analyses are similar to the data for

---

E-mail address: bojinova@uctm.edu (D. Bojinova).

0040-6031/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0040-6031(03)00145-X

the phase composition of the system CaO-P_2O_5-SiO_2 [5].

The aim of this study was to establish the influence of the additive's quantity of Si-containing waste, the temperature and the mechanical activation on the P_2O_5 solubility in various extracting agents. Using chemical and XRD analyses the phase transformation in the calcined products was established.

2. Materials and methods

2.1. Materials

In this investigation a commercial Tunisian phosphorite (TP) a fraction below 0.63 mm was used. The TP contains apatite mineral, carbonates, alumosilicates, glauconite, limonite and clay minerals. The average chemical content of the TP is shown in Table 1.

Si-containing waste, named "Medet's steryl" (MS), was obtained during the copper ore enrichment in "Medet" Co. in Bulgaria.

K–Na feldspar; orthoclase—$K(AlSi_3O_8)$; albite—$Na(AlSi_3O_8)$; andesine-plagioclase—$(Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2){\cdot}2(CaO{\cdot}Al_2O_3{\cdot}2SiO_2)$; biotite—$K_2O{\cdot}6FeO{\cdot}Al_2O_3{\cdot}SiO_2{\cdot}H_2O$; quartz-$SiO_2$; chalcopyrite—$CuFeS_2$; and clay materials. The average chemical composition of the used TP and MS is presented in Table 1.

2.2. Analyses

The apatite mineral and the mixtures were analyzed [6] spectrophotometrically—phosphorus (vanadomolybdate yellow complex) and iron (sulphosalicylic acid complex); titrimetry with $KMnO_4$ for calcium, atom absorption spectrophotometry (AAS) for magnesium, flame spectrophotometry for potassium and sodium, weight analysis for silicon, ion selective electrode for fluorine and volumetric analysis for CO_2.

XRD was carried out with DRON UM-1 equipment using Cu Kα radiation in the range of angles 5–40°, rate $1^\circ\,\mathrm{min}^{-1}$.

2.3. Mechanical activation

The mechanical activation of TP, as well as of its mixtures with MS, was carried out in a planet mill type "Pulverisete" 5 using metal balls with 20 mm diameter. The mass ratio between the material and the mill bodies was 1:20. The time for the activation was 1 h and the rotation intensity used was 290 rpm.

3. Experimental

Samples of 5 g non-activated (NP) and activated (AP) Tunisian phosphorite, as well as mixtures of TP with MS—not-activated (NM) and activated (AM), were placed in a corundum crucible and calcined in a furnace preliminary heated to the corresponding temperature for 1 h. The experiments were carried out with three ratios of TP and MS: 1:0.05; 1:0.10; 1:0.25, correspondingly where the additives quantity was 5, 10 and 20% to the total mass of the mixture. The samples were heated at the temperature 200, 400, 600, 800, 1000 and 1200 °C, respectively, cooled slowly and ground if necessary. The obtained materials were analyzed for the content of the total ($P_2O_{5\mathrm{tot.}}$) and assimilable P_2O_5. The availability of phosphorus for plants was estimated by its solubility in 2% citric acid ($P_2O_{5\mathrm{c.s.}}$), neutral ammonium citrate solution ($P_2O_{5\mathrm{am.c.}}$) and 2% formic acid [6]. Simultaneously, a part of the extract for the determination of the soluble P_2O_5 in citric acid was treated with 20% HCl at heating for 10 min. After that the determination was similar to that without treatment with HCl. The analysis of P_2O_5 was made spectrophotometrically based on the produced with vanadomolybdate yellow complex.

Table 1
Chemical composition of the materials (mass%)

Material	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SiO_2	F	CO_2	H_2O	Organic
TP	29.4	50.1	0.9	0.8	0.5	2.0	0.2	2.0	3.5	4.8	1.2	1.4
MS	–	1.3	1.6	9.9	4.2	1.1	2.2	78.2	–	–	1.0	0.5

Table 2
Composition of the obtained mixtures

Additive		Chemical composition of the mixture (mass%)									Mole ratio	
%	Mass ratio	P_2O_5	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SiO_2	F	R^*	SiO_2/P_2O_5
5	1:0.05	28.9	47.6	0.9	1.3	0.7	0.3	1.9	3.7	3.3	3.1	0.5
10	1:0.10	26.6	45.2	0.96	1.5	0.9	0.4	1.9	7.1	3.2	2.6	0.9
20	1:0.25	24.3	40.3	1.01	2.6	1.2	0.6	1.8	15.6	2.8	1.8	1.7

$R^* = M_2O + MeO + Me_2O_3/P_2O_5 + SiO_2$, where: Me_2O—content of K_2O and Na_2O (mol), MeO—content of CaO and MgO (mol), Me_2O_3—content of Al_2O_3 and Fe_2O_3 (mol).

Table 3
Chemical composition of the obtained products after thermal treatment of (NP and AP) (mass%)

T (°C)	$P_2O_{5tot.}$		$P_2O_{5c.s.}$		$P_2O_{5c.s./HCl}$		$P_2O_{5am.c.}$		$P_2O_{5f.s.}$	
	NP	AP	NP	AP	NP	AP	NP	AP	NP	AP
–	29.41	29.32	1.16	14.06	10.28	15.15	4.68	15.44	20.71	20.56
200	29.74	29.50	9.27	14.36	9.46	15.11	4.37	13.82	19.28	20.89
400	29.92	29.32	9.02	14.26	9.21	15.17	4.27	10.93	17.70	20.85
600	31.12	29.96	8.05	11.95	8.23	12.98	3.79	6.26	10.82	15.23
800	31.50	30.01	6.15	9.88	6.36	10.41	3.58	6.00	7.30	7.96
1000	31.90	30.22	6.11	6.98	6.72	6.60	3.52	5.80	5.73	7.38
1200	32.38	32.12	5.82	5.14	6.78	6.74	3.55	5.50	5.22	7.23

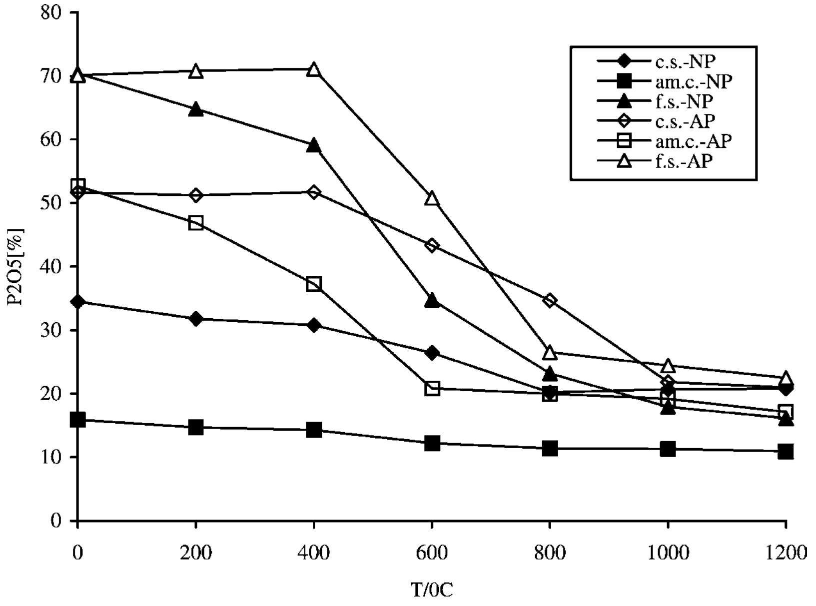

Fig. 1. Extraction degree of P_2O_5 in assimilable form at thermal treatment of Tunisian phosphorite (NP and AP).

Table 4
Chemical composition of the obtained products after thermal treatment of mixtures (mass%)

T (°C)	$P_2O_{5tot.}$		$P_2O_{5c.s.}$		$P_2O_{5c.s./HCl}$		$P_2O_{5am.c.}$		$P_2O_{5f.s.}$	
	NM	AM	NM	AM	NM	AM	NM	AM	NM	AM
MS—5%										
–	29.22	28.92	9.22	13.92	9.50	15.97	4.22	15.44	17.70	17.64
200	29.30	29.00	9.22	12.32	9.36	15.62	4.22	14.91	17.37	17.28
400	29.40	29.20	9.47	12.36	9.47	14.44	4.21	11.04	16.52	17.08
600	29.45	29.50	7.90	12.04	8.28	12.63	3.74	10.42	10.60	14.75
800	29.80	29.50	6.95	10.02	7.12	10.57	3.68	9.44	6.47	10.53
1000	30.50	29.70	6.24	8.85	6.60	10.24	3.31	2.79	6.62	7.40
1200	31.50	31.76	3.70	3.24	3.73	3.57	2.59	2.50	3.50	3.70
MS—10%										
–	26.80	26.61	9.40	13.70	9.55	16.00	6.90	13.96	17.00	16.18
200	26.85	26.77	9.35	12.90	9.51	15.08	6.76	11.80	16.28	16.54
400	26.93	26.85	9.02	12.51	9.46	13.35	6.89	10.94	15.80	16.50
600	27.00	26.90	8.37	12.40	8.99	13.47	7.00	9.57	11.33	14.14
800	27.50	27.14	6.71	10.66	7.39	11.16	6.48	9.73	8.00	9.51
1000	27.80	27.36	5.89	10.17	6.63	1.05	6.00	6.20	7.60	9.47
1200	30.50	30.75	3.05	3.30	3.58	3.55	3.28	3.24	3.55	3.04
MS—20%										
–	24.70	24.50	10.20	13.40	10.20	16.17	8.20	12.74	15.20	15.04
200	24.85	24.80	10.05	12.68	10.12	15.00	8.00	11.72	14.50	14.87
400	25.20	25.00	9.78	12.10	10.03	13.82	8.20	11.14	14.20	14.87
600	25.70	25.50	8.58	12.00	8.83	13.00	7.44	10.82	12.20	14.31
800	26.20	25.90	7.15	11.33	7.48	11.85	6.44	9.90	8.54	10.15
1000	26.80	26.50	7.14	10.75	7.37	11.58	6.14	6.50	7.90	8.20
1200	27.80	27.20	3.50	3.68	3.80	3.85	3.36	3.88	3.23	3.87

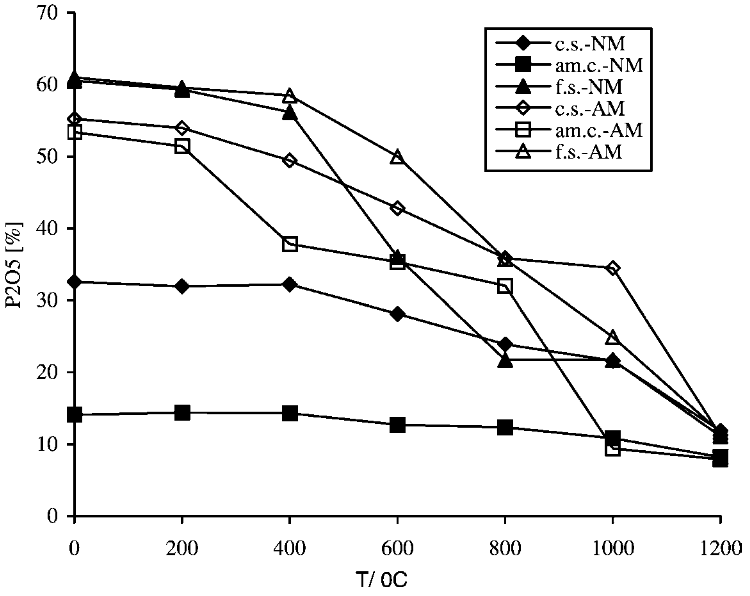

Fig. 2. Extraction degree of P_2O_5 in assimilable form at thermal treatment of mixtures with 5% MS additives.

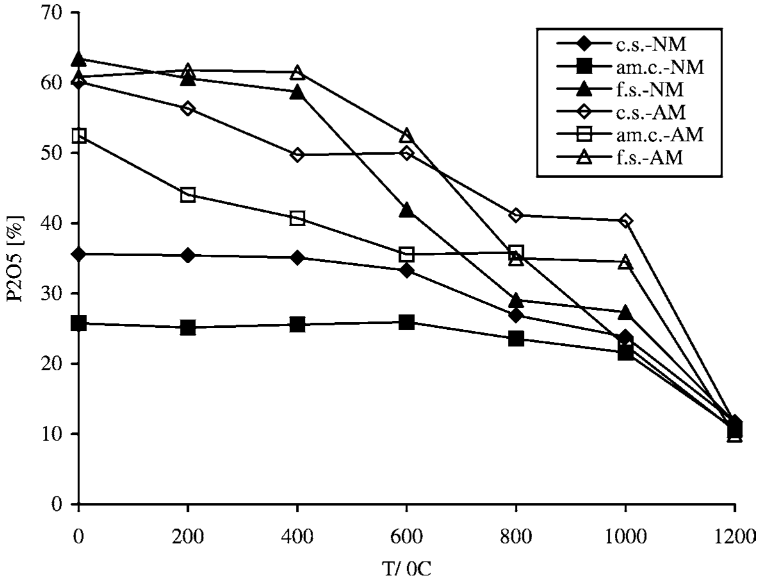

Fig. 3. Extraction degree of P_2O_5 in assimilable form at thermal treatment of mixtures with 10% MS additives.

On the basis of the results obtained for P_2O_5 content assimilable in the extracting agents mentioned before, the extraction degree (α%, w/w) was calculated, compared to the total content of P_2O_5 in the calcined samples.

Both the raw materials and their calcined mixtures were subjected to XRD analysis. XRD patterns were obtained with DRON UM-1 equipment using radiation in the range of angles 5–30 θ, step size 0.

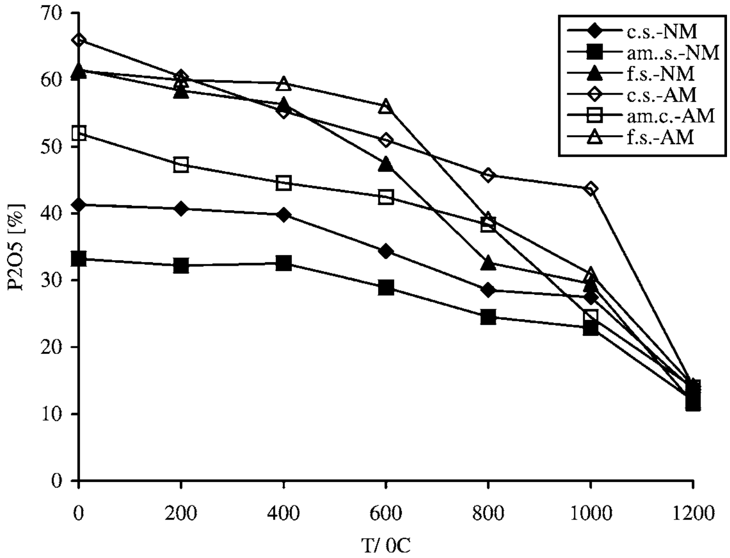

Fig. 4. Extraction degree of P_2O_5 in assimilable form at thermal treatment of mixtures with 20% MS additives.

4. Results and discussion

The content of the obtained mixtures was calculated using the chemical composition of TP and MS and the corresponding mass ratios between them (Table 2). The content of the obtained products before and after the thermal treatment of NP and AP related to the total and assimilable P_2O_5 is shown in Table 3. Obviously the content of the total P_2O_5 increases with the increase of the temperature from 200 up to 1200 °C regardless if TP was activated or not.

The values of the assimilable P_2O_5 in the case of the activated TP are higher compared to non-activated TP irrespective of the extracting agent's type, as well as of the temperature of heating. The highest values for P_2O_5 are achieved when formic acid was used. A tendency of decreasing of the assimilable P_2O_5 with the increase of the temperature was established regardless of the extracting agent used.

The extent of P_2O_5 transformation with various extracting agents depending on the temperature is shown in Fig. 1. There is a tendency of decreasing in the extent of P_2O_5 transformation into assimilable form independently of the agent's type.

In Table 4 and Figs. 2–4, respectively, the results from the investigations on the influence of the MS additive's quantity on P_2O_5 transformation into assimilable form during the thermal treatment of the mixtures with TP are shown. To establish the role of the mechanical treatment, the experiments were carried out with NM and AM at similar ratios of TP:MS as shown in Table 2.

A common tendency is the decreasing of the extent of P_2O_5 transformation into assimilable form with the increase of the temperature regardless of the extracting agent and at constant quantity of the additive in the mixtures. The values for P_2O_5 (soluble in citric acid with/without hydrolysis and soluble in citrate) for the activated TP, as well as for its mechanically activated mixtures with MS, are higher compared to non-activated TP and its corresponding mixtures with MS. The extent of extraction of the soluble in citric acid P_2O_5 is 16.7% higher for the activated TP compared to NP. This difference increases for the activated mixtures and it is 25% for the highest quantity of the additive (20%). It keeps the highest value also for the mixtures with 5% additive (22%) when the temperature increases up to 200 °C and gradually decreases with further increase of the temperature. The highest extent of P_2O_5 transformation (66%) into soluble citric acid form was achieved for the activated mixture of TP and MS (20%). The similar tendency has been observed also for the citrate soluble P_2O_5 but the differences were higher. They varied from 18.8 to 39.2%. The highest value achieved was for the activated

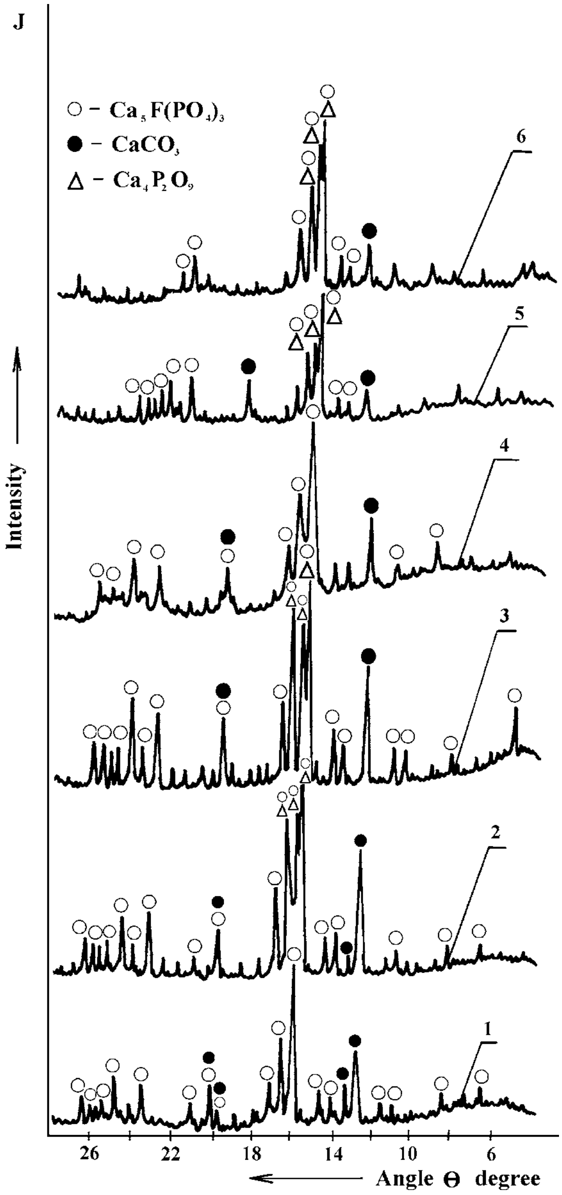

Fig. 5. XRD patterns for TP. (1) NP; (2) NP (800 °C); (3) NP (1000 °C); (4) AP; (5) AP (800 °C); (6) AP (1000 °C).

mixture with 5% additive and the lowest—for that with 20% additive. When the treatment temperature increases, α-$P_2O_{5\mathrm{am.c.}}$ decreases more slightly. The values for the extent of P_2O_5 transformation in citrate soluble form for the activated TP and its mixtures with MS do not differ drastically (52–53%).

Strongly expressed increase of the extent of P_2O_5 transformation in a citric acid soluble form, as well as in citrate soluble form, in the case of AP compared to AP shows that the mechanical activation results in changes in the phosphates crystal lattice. The influence of the mechanical activation on the crystal's surface

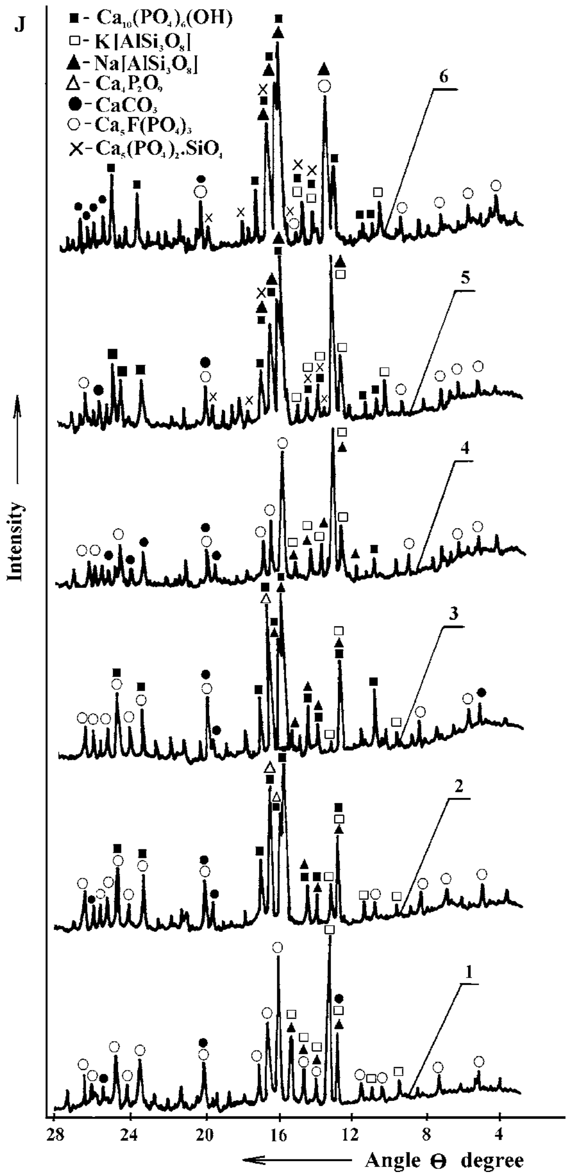

Fig. 6. XRD patterns for NM, containing 5 and 20% MS. (1) 5% MS; (2) 5% MS (800 °C); (3) 5% MS (1000 °C); (4) 20% MS; (5) 20% MS (800 °C); (6) 20% MS (1000 °C).

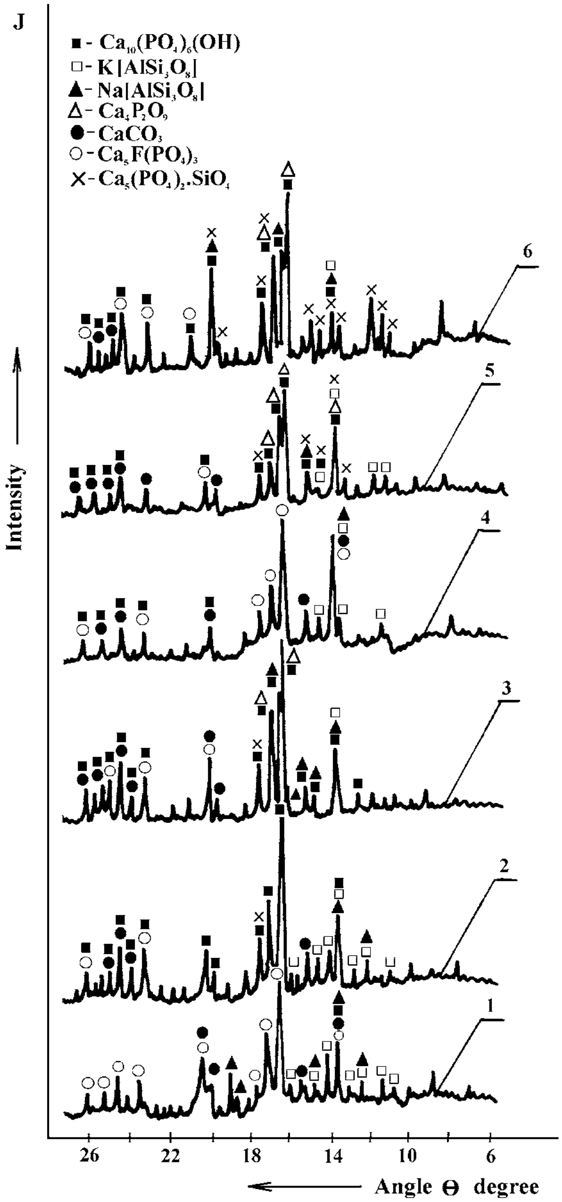

Fig. 7. XRD patterns for AM, containing 5 and 20% MS. (1) 5% MS; (2) 5% MS (800 °C); (3) 5% MS (1000 °C); (4) 20% MS; (5) 20% MS (800 °C); (6) 20% MS (1000 °C).

was stated in some publications too [7–9]. X-ray analysis of the mixtures and of the products after calcination was carried out for the establishment of the processes thus occurred in the system.

In Fig. 5, position 1 representing NP and position 4 (AP), the characteristic diffraction maxima for carbonate fluorapatite can be seen clearly at d (Å): 5.30; 4.61; 4.04; 3.87; 3.45; 3.34; 2.79; 2.68; 2.62; 2.28; 2.24; 2.12; 2.06; 1.93; 1.88; 1.82; 1.79; 1.76; 1.74; 1.72. There is a splitting of the maximum at $d = 2.79$ Å in two reflexes at 2.81 and 2.77 Å, respectively (positions 2, 3, 5 and 6). They differ slightly in their intensities at 800 and 1000 °C. This change is concerned with a transformation of $Ca_5F(PO_4)_3(CO_3)$ in $Ca_5(PO_4)_3(OH)$ and $Ca_4P_2O_9$. From Figs. 6 and 7 representing the patterns NM and AM of TP and MS (5 and 20%) after thermal treatment at 800 and 1000 °C, a conclusion can be made that as a result of the heating at these temperatures chemical interactions occur leading to a creation of new phases, such as $Ca_5(PO_4)_3(OH)$, $Ca_5(PO_4)_2{\cdot}SiO_4$ and $Ca_4P_2O_9$.

The comparison of the data from the chemical analysis and those of X-ray phase analysis confirms this fact. The data show that the largest difference for α-$P_2O_{5\mathrm{c.s.}}$ between the initial mixture irrespective of the additive's content and a mixture without an additive was achieved at 1000 °C. This difference increases with an increase of the percentage content of the additive in the mixture. As an example for 5% additive, the difference is 12.6% and for 20% MS—21.8%. A similar tendency was observed also for α-$P_2O_{5\mathrm{am.c.}}$ but these more significant differences start at 600 °C and are saved up to 800 °C. In the presence of MS additive and during their thermal treatment solid solutions probably are formed between $Ca_3(PO_4)_2$ and β-Ca_2SiO_4, such as silikocarnotite $[Ca_5(PO_4)_2{\cdot}SiO_4]$ and negelshmite $[Ca_7(PO_4)_2{\cdot}(SiO_4)_2]$, as well as $Ca_4P_2O_9$. They are soluble in citric acid and neutral solution of ammonium citrate. According to X-ray analysis they are recorded at 200 °C but their diffraction maxima are most intensive at 800 and 1000 °C. The strong decrease in the most characteristic bands of orthoclase and albite, which are the main minerals in the Medet's steryl structure, at combined thermal treatment with TP shows that they are involved in chemical interactions with it. It is quite possible that K^+ and Na^+ are inserted in the crystal's lattice of β-$Ca_3(PO_4)_2$ because of cation's vacancies. This replacement of Ca^+ with K^+ and Na^+ is limited. It depends on the number of the "cation's vacant ions", and according to X-ray and IR spectroscopy studies of similar systems [10,11], does not result in a change of β-$Ca_3(PO_4)_2$ structure. In this way the alkaline varieties of hydroxylapatite: dehrnite $[(Ca,Na)_{10}(PO_4)_6(CO_3)(OH)_2]$ and lewistonite $[(Ca,K,Na)_{10}(PO_4)_6(CO_3)(OH)_2]$ are formed. The diffraction maxima of these two compounds coincide with those of hydroxylapatite, silikocarnotite and negelshmite. Dehrnite and lewistonite are compounds also soluble in citric acid and ammonium citrate solution.

References

[1] R.L. Barret, W.L. Mc Coughey, Am. Miner. 28 (1942) 680.
[2] M. Veiderma, K. Tonsuaadu, Acta Polytech. Scand., Chem. Tech. Series 239 (1996) 3.
[3] K. Tonsuaadu, K. Rimm, Proc. Estonian Acad. Sci. Chem. 43 (1994) 137.
[4] K. Tonsuuadu, M. Veiderma, Proc. Estonian Acad. Sci. Chem. 41 (1992) 157.
[5] B. Baatarsuh, V.N. Golubev, B.I. Lazoryak, R.G. Aziev, Chimicheskaya Promishlenost 11 (1991) 23 (in Russian).
[6] F.N. Kelman, Y.B. Brutskus, R.k. Osherovich, Methods of Analysis in Manufacture of Sulphuric Acid and Phosphate Fertilizers, Khimiya, Moskow, 1965, p. 392.
[7] V.F. Karmashof, Himicheskaya pererabotka phosphotitov, Khimiya, Moskow, 1983, p. 58.
[8] I. Dombalov, A. Toneva, Y. Pelovsky, I. Gruncharov, Annual-book of Higher Institute of Chemical Technology, vol. 31, 1992, p. 139.
[9] I. Dombalov, A. Toneva, Y. Pelovsky, I. Gruncharov, Annual-book of Higher Institute of Chemical Technology, vol. 31, 1992, p. 147.
[10] V.N. Golubev, S.V. Prohorenko, B.I. Lazoryak, R.G. Aziev, Chimicheskaya Promishlenost 3 (1988) 16 (in Russian).
[11] S.U. Oralkov, B.I. Lazoryak, R.G. Aziev, J. Neorganicheskoi Chimii. 33 (1988) 73 (in Russian).