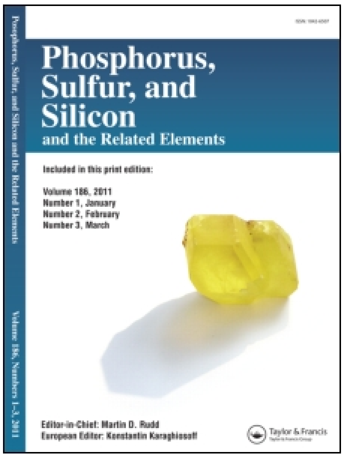

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COMPOSITION AND PROPERTIES OF THERMOPHOSPHATES FROM APATITE AND ALUMINOSILICATES

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Decomposition of Kovdor apatite at 1350°C in the mixture with or without H_3PO_4 and with aluminosilicates (glauconite, nepheline, pseudoleicite) and the solubility in 2% citric acid solution of the calcined phosphate components (P, Ca, Mg, Fe, K, Na, Si) have been studied by chemical and X-ray powder diffraction analysis. The solubility of P_2O_5 is 56–73% of its total content in the mixture with G, 42–78% with N and 53–82% with P, as the result of formation of solid solution α-$Ca_3(PO_4)_2$ – α-Ca_2SiO_4 and β-$(Ca, Mg)_3(PO_4)_2$. The formation of more fluorine-rich apatite during heating was established.

Key words: Apatite; aluminosilicate; calcined phosphate; 1350°C, phase composition; solubility.

INTRODUCTION

The object of this work was to study the influence that addition of different natural aluminosilicates, accompanying phosphates in their deposits, has on the composition and solubility of the products obtained by thermal processing in solid state of Kovdor apatite. The purpose was to obtain a phosphorus fertilizer without the use of expensive synthetic reagents.

EXPERIMENTAL

The raw materials used were concentrate of apatite from a Kovdor deposit, whose apatite mineral corresponds to the formula $Ca_{10}(PO_4)_6 \cdot F_{0.6}(OH)_{1.4}$, and concentrates of glauconite (G)—$K_2O \cdot 4(MgO, FeO, Fe_2O_3, Al_2O_3) \cdot 10SiO_2 \cdot 3H_2O$ from an Estonian phosphorite deposit, of nepheline (N)—$3Na_2O \cdot K_2O \cdot 4Al_2O_3 \cdot 8SiO_2$ from a Kola apatite deposit and of pseudoleicite (P)—mixture of $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ and $K_2O \cdot Al_2O_3 \cdot 2SiO_2$ from an East-Siberian Oshurkovo apatite deposit. Their chemical composition is given in Table I. In the apatite concentrate the content of apatite mineral is 87.8% and the main impurity minerals are calcite, dolomite and forsterite. In the experiments chemically pure phosphoric acid (37.5% P_2O_5) was used.

The samples (5 g) of ground mixtures of apatite and aluminosilicate with or without H_3PO_4 were calcined at 1350°C in a Pt crucible (layer thickness 7–10 mm) in an electrical tube kiln with diameter 22 mm, passing air containing up to 20% of water vapor in an amount 30 l/h through it, then rapidly cooled in air.

The heating temperature (1350°C) was chosen by thermograms[1] (according to which decomposition of apatite begins above 1200–1250°C), but it must be lower than the temperature at which the mixtures begin to melt.

The quantity of additives was limited also, as aluminosilicates lower the melting temperature of the mixtures. The advisable molar ratios are for $CaO:P_2O_5 > 2.9–3.2$ and for $SiO_2:P_2O_5 > 0.21–0.25$, established by the results obtained with model mixtures.[2]

The availability of the products for plants was estimated by their solubility in a citric acid solution. The ground calcined products were treated with 2% citric acid solution for 30 min at 20°C. The ratio of the sample and the solution masses was 1:200. The content of the mixture components (P, Ca, Mg, Fe, Na, K and F) was determined by chemical, AAS, spectro-photometric and ion-selective methods.

TABLE I

Chemical composition of initial materials, %

Mineral	P_2O_5	CaO	MgO	R_2O_3	SiO_2	F	CO_2
Kovdor apatite	36.5	51.1	2.7	0.7	1.4	1.0	3.4
	Na_2O	K_2O	MgO	Fe_2O_3	Al_2O_3	SiO_2	
Glauconite	0.1	8.9	4.4	20.3	10.7	51.1	
Nepheline	11.4	6.3	0.2	3.3	22.2	54.3	
Pseudoleicite	0.4	15.0	0.3	1.1	21.5	55.7	

X-ray powder diffraction was used to study the phase composition of the calcined products and their insoluble residue in 2% citric acid solution. Diffraction data were obtained with DRON-4 equipment using Cu radiation and flat diffracted beam monochromator (graphite). Step-scan data were collected with step size 0.03 deg from 20° to 50° 2-theta. Unit-cell parameters for apatites were refined using standard least-squares procedure. Quantitative amounts of apatite were determined by internal standard method. Corundum (Al_2O_3) was chosen for a standard and added to samples in weight fraction 1:4. Because of line overlapping problems only one peak intensity from both phases was used for calculations.

RESULTS AND DISCUSSION

The chemical composition of the products obtained by heating at 1350°C during 2 hours is presented in Table II. The molar ratio $CaO:P_2O_5$ in apatite and in the mixtures without H_3PO_4 is 3.60–3.75. In the mixtures where H_3PO_4 was added, the $CaO:P_2O_5$ ratio varies 3.13–3.47. The molar ratio of $SiO_2:P_2O_5$ varies from 0.22 to 0.35, depending on the content of SiO_2 in the added aluminosilicates and the quantity of H_3PO_4 added.

The content of the components that increase the temperature of $\beta \rightarrow \alpha\text{-}Ca_3(PO_4)_2$ transformation[3–6] and, therefore, decrease the solubility of calciumphosphate, is the highest in the mixtures with G (MgO 2.6–2.8%, Fe_2O_3 1.2–1.7%, Al_2O_3 0.6%). In the same mixture, the content of alkaline metals facilitating decomposition of apatite, is the lowest (K_2O 0.3%). In the mixtures with N and P the sum of K_2O + Na_2O is higher (0.8–1.0%) and the content of MgO is 1.9–2.3%, Fe_2O_3 0.2–0.3% and Al_2O_3 1.3%.

The fluorine content varies from 0.9 to 0.4% in heated mixtures. The amount of fluorine volatilized (Table II) increases significantly if H_3PO_4 is added. It doubles in the mixture with P, rises 5-fold time in the mixture with N and 10-fold in the mixture with G.

The solubility data of the calcined products in 2% citric acid solution are presented in Table III. The relative solubility of P_2O_5 increases from 21.5% of apatite

TABLE II

Chemical composition of calcined products (1350°C, 120 min)

	Admixture (% to apatite mass)		Composition (%)									Volatilized (rel.%)	Molar ratio	
Nº	P_2O_5	Silicate	P_2O_5	CaO	MgO	Fe_2O_3	Al_2O_3	K_2O	Na_2O	SiO_2	F	F	CaO: P_2O_5	SiO_2: P_2O_5
1	0	0	37.8	53.6	2.8	0.5	<0.1	0.1	<0.1	1.5	0.9	10	3.60	0.11
2	2.5	0	40.0	52.2	2.7	0.5	<0.1	0.1	<0.1	1.5	0.9	23	3.31	0.09
3	0	6 G	36.9	54.6	2.6	1.2	0.6	0.3	<0.1	4.5	0.9	4	3.75	0.29
4	2.5	6 G	38.3	52.4	2.7	1.3	0.6	0.3	<0.1	3.8	0.6	42	3.47	0.23
5	3.5	6 G	39.7	50.6	2.8	1.7	0.5	0.3	<0.1	3.7	0.7	31	3.23	0.28
6	0	6 N	36.7	52.1	1.9	0.2	1.3	0.3	0.7	5.2	0.9	6	3 60	0.34
7	2.5	6 N	38.6	51.6	1.9	0.2	1.3	0.3	0.7	4.7	0.7	32	3.39	0.29
8	3.5	6 N	39.2	49.9	1.9	0.1	1.2	0.3	0.8	4.7	0.4	60	3.23	0.28
9	0	6 P	36.7	52.2	2.4	0.3	1.3	0.8	<0.1	5.5	0.8	17	3.61	0.35
10	2.5	6 P	38.2	51.7	2.3	0.3	1.3	0.8	<0.1	5.5	0.6	39	3.43	0.34

TABLE III
Solubility of calcined products in 2% citric acid solution

Sample Nº*	Solubility in 2 % citric acid (rel. %)					Insoluble residue (%)
	P_2O_5	CaO	MgO	Fe_2O_3	SiO_2	
1	21.5	31.1	80.1	63.6	93.0	73.6
2	32.8	33.7	71.8	23.5	93.0	66.2
3	55.7	60.6	67.2	9.6	86.7	41.8
4	73.0	74.3	72.1	19.7	84.2	27.8
5	55.1	55.7	66.0	54.2	78.4	42.8
6	42.2	50.5	68.4	20.0	75.0	53.8
7	73.6	72.6	86.0	40.0	77.0	27.0
8	78.0	78.7	85.6	52.2	72.3	23.9
9	52.9	58.0	62.5	20.0	80.0	44.5
10	82.0	82.2	84.7	52.1	90.9	18.9

* Sample numbers according to Table II.

to 32.8% in the mixture with H_3PO_4 and to 42–56% in the mixtures with aluminosilicates. In the mixtures with both, H_3PO_4 (2.5%) and aluminosilicates, the solubility of P_2O_5 increases up to 76% (with G), 73% (with N) and 82% (with P), as a result of an accelerated decomposition of apatite (Table IV). The lower solubility (55.1% P_2O_5) of the calcined product of the mixture with G and the bigger amount of H_3PO_4 (3.5%) is the result of partial melting of the mixture, which hinders volatilization of F and therefore inhibits decomposition of apatite (Table IV). The formation of the liquid phase is the result of melting of Ca-Mg-phosphates[7] and of G at 1280°C.

When the heating time was prolonged, the solubility of P_2O_5 in the mixtures with H_3PO_4 rose (Figure 1), but it did not reach the value obtained in the experiments with the model mixtures (up to 86% with G and 97–98% with N or P).[2]

The solubility of phosphorus increases proportionally to the decrease of fluorine content in the calcined products (Figure 2). At the same time, it was established,

TABLE IV

Phase composition of calcined products and the apatite unit-cell parameter a

Sample Nº*	Apatite (± 3 %)	Phosphates(± 3 %)		Insoluble silicates (%)	F content in apatite (%)	a of apatite, ±0.002 Å
		α + β	Insoluble			
1	75	24		<1	1.0 ±0.05	9.400
2	57	42	9	<1	1.6 ±0.1	9.400
3	40	59	<1	1	2.3 ±0.2	
4	23	76	4	1	2.6 ±0.3	9.385
5	25	73	16	2	2.8 ±0.3	
6	45	53	6	2	2.0 ±0.1	9.394
7	17	81	8	2	4.1 ±0.6	9.382
8	13	84	8	3	3.1 ±0.6	
9	40	58	2	2	2.0 ±0.1	9.394
10	12	87	6	1	5.0 ±1.0	9.381

* Sample numbers according to Table II.

that the content of fluorine in residual apatite is the higher, the lower the amount of apatite in the products is (Table IV), which is due to the substitution of F^- for OH^- in the OH,F-apatite structure.[7,8] The increase of F content in the apatite crystal lattice was proved by chemical and quantitative X-ray diffraction analysis, as well as by the decrease of the unit-cell parameters of apatite[9] (Table IV). The increase of fluorine content in apatite makes it more stable, which explains the deceleration of the defluorination rate and the rise of P_2O_5 solubility.

The solubility of CaO is approximately equal to the solubility of P_2O_5, as the amount of soluble calciumphosphates in the product depends on the decomposition rate of the apatite.

The solubility of Mg and Fe is generally higher than the solubility of P and Ca and usually increases in accordance with the extent of apatite decomposition.

The solubility of SiO_2 varies from 72 to 93 rel.%. The content of insoluble silicates in the calcined products is about 1–3% (Table IV).

During calcination partial volatilization of K_2O (10–40%) and Na_2O (<10%)

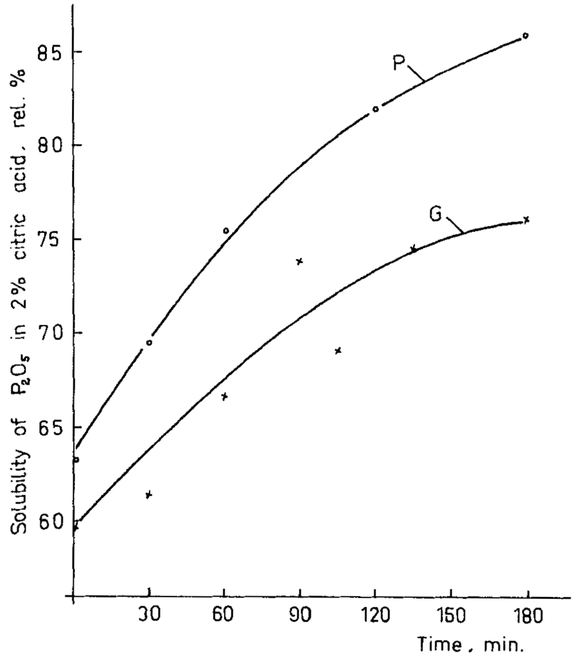

FIGURE 1 Dependence of P_2O_5 solubility in 2% citric acid solution on the duration of heating of the mixtures 4 and 10 (Tables II) at 1350°C.

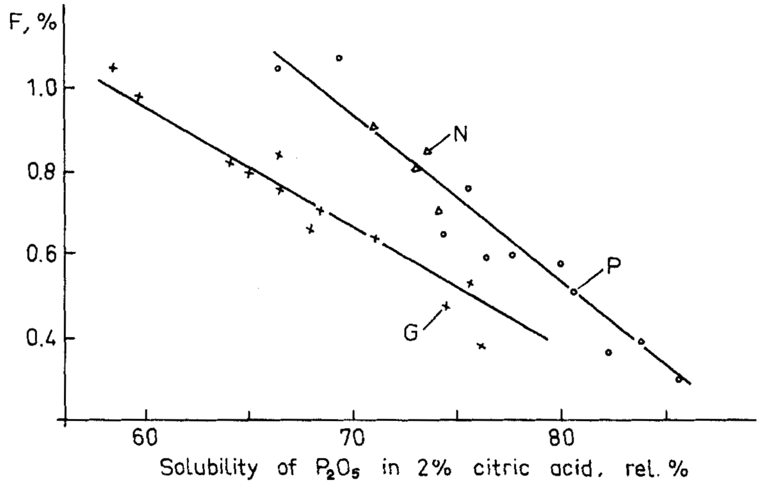

FIGURE 2 Dependence of P_2O_5 solubility in 2% citric acid solution on the fluorine content in the calcined product of the mixtures with glauconite (G) and pseudoleicite (P).

takes place. The alkaline metals contained in the products are completely soluble in 2% citric acid.

As a result of the analysis of X-ray diffraction patterns of the calcined products (Figure 3), it was established that they contain hydroxy-fluoroapatite [OH,F-apatite] with characteristic peaks at d = 2.80, 2.78, 2.71 Å, solid solutions of α-

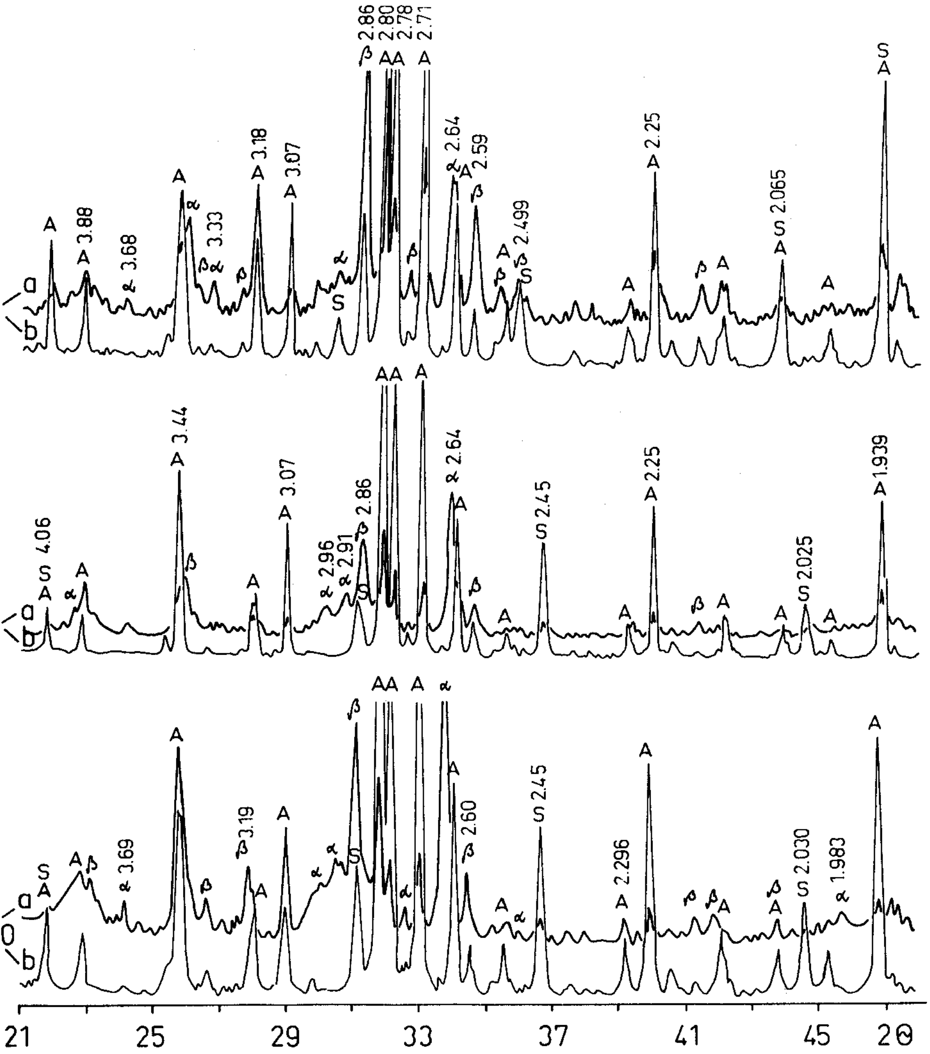

FIGURE 3 X-ray diffraction patterns in the range of angles 21–47° 2-theta for the samples, 4, 7 and 10 (Table II). (a) calcined product, (b) insoluble residue in 2% citric acid solution. A—OH, F-apatite; α—solid solution of α-$Ca_3(PO_4)_2$ + α-Ca_2SiO_4; β—$(Ca, Mg)_3(PO_4)_2$; S—$(Ca, Mg)\cdot(Al_2O_3, Fe_2O_3)\cdot 2SiO_2$.

$Ca_3(PO_4)_2$-α-Ca_2SiO_4 [α-Ca_3P], d = 2.65, 2.92, 2.98 Å; β-$(Ca, Mg)_3(PO_4)_2$ [β-$(Ca, Mg)_3P$], d = 2.86, 2.59, 2.74 Å and a silicate with variable composition (CaO, MgO)·(Al_2O_3, Fe_2O_3)·$2SiO_2$ [S], d = 2.45–2.49, 2.87–2.93, 2.030–2.067 Å (lattice constant a=b=c = 8.110–8.270 Å). The latter was established as an HCl-insoluble residue of the 2%-citric-acid-insoluble residue of the calcined products.

At the diffraction patterns of the residues insoluble in citric acid solution (Figure 3), the disappearance of the peaks for α-Ca_3P and the increase of the relative intensities of the peaks for OH, F-apatite and S, in respect to the β-$(Ca, Mg)_3P$ peaks intensities, were observed. Therefore, the soluble part of the calcined products consists mainly of α-Ca_3P and β-$(Ca, Mg)_3P$. There is the possibility of forming citric acid soluble calcium silicophosphates also by heating, but as these and the solid solutions of α-$Ca_3(PO_4)_2$ – α-Ca_2SiO_4 have the same crystal structure, their identification is impossible in the same mixtures.

Lazoriak and Golubev have shown[10,11] that the solubility of calcium silicophosphates does not decrease when Ca is partially replaced by Mg, Al, Fe, Na, etc. atoms in their crystal structure, if the structure of β-K_2SO_4 remains. On the contrary, the solubility of compounds with the β-$Ca_3(PO_4)_2$ crystal structure decreases, when substitutions of the above-mentioned atoms for Ca take place. The results of our study are in good correlation with these data.

As in the calcined products of the mixtures with H_3PO_4 phosphates of β-$Ca_3(PO_4)_2$ structure (beside apatite) dominate. The influence of Mg, Al and Fe is essential for their solubility. Therefore, the higher the content of Mg and Fe in the mixture (mixtures with G), the lower the solubility of P_2O_5 to the same extent of the decomposition of apatite and at the same SiO_2:P_2O_5 molar ratio in the mixture.

The different influence of various aluminosilicates on the decomposition of apatite and on the solubility of the product became clear. The comparison of the phase composition of the mixtures (Table IV) shows that P has the strongest influence on decomposition of apatite at 1350°C. The residual apatite content in the calcined product of the mixture without H_3PO_4 is 40% and in the mixture with H_3PO_4 (2.5%) 12%. At the same time, these figures in the mixtures with N are 45 and 17% and with G 40 and 23%. The differences could be explained not only by the differences in chemical composition discribed above, but also by the different thermal stability of aluminosilicates. N melt at 1230°C, in G the first melt forms at 1120°C and it melts completely at 1280°C, but P is stable up to 1400°C. On the one hand, the melt interacts more easily with apatite, but, on the other hand, the partial melting by sintering processing hinders the fluorine volatilization, which leads to a more stable apatite formation than was mentioned above.

CONCLUSIONS

In the mixtures of Kovdor apatite with aluminosilicates (glauconite, nepheline and pseudoleicite), at 1200°C decomposition of OH, F-apatite begins. Formation of α-$Ca_3(PO_4)_2$ – α-Ca_2SiO_4 solid solution. β-$(Ca, Mg)_3(PO_4)_2$, Ca, Mg, Al, Fe-silicate and fluorine rich apatite takes place at the reactions in solid state as well as by interaction with liquid phase. The extent of the decomposition of apatite is influenced by the choice and amount of aluminosilicate, the temperature, the time of heating and the amount of H_3PO_4 added.

The availability of the calcined products for plants depends mostly on the extent of decomposition of apatite, as well as on the content of Mg, Al, Fe and the molar ratios of CaO:P_2O_5 and SiO_2:P_2O_5 in the mixtures.

Nepheline and pseudoleicite proved to be more suitable additives in comparison with glauconite for getting a citric acid soluble fertilizer by hydrothermal sintering processing of Kovdor apatite.

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