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THERMOPHOSPHATES ON THE BASIS OF APATITE AND ALUMINOSILICATES

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Abstract Composition and solubility of thermo-phosphates obtained from natural apatites and aluminosilicates (glauconite, nepheline, pseudo-leicite) have been studied.

The solubility of phosphorus in the products obtained by solid phase hydrothermal processing of phosphate rock meets the requirements set up for feed phosphates but not those for fertilizers. Phosphorusⁱⁿ products is mainly present in the form of $\beta\text{-Ca}_3(\text{PO}_4)_2$ ¹. The product solubility can be increased by using natural aluminosilicates which often accompany phosphates in their deposits². The object of this work was to study the effect of different aluminosilicates on the composition and solubility of the heating products of apatite. Simultaneously the same problems were studied in model systems from pure reagents³.

Kovdor and Kola apatite were used as raw materials and glauconite ($\text{K}_2\text{O} \cdot 4(\text{MgO}, \text{FeO}, \text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3) \cdot 10\text{SiO}_2 \cdot 3\text{H}_2\text{O}$) from Estonian phosphorite deposit, nepheline ($3\text{Na}_2\text{O} \cdot \text{K}_2\text{O} \cdot 4\text{Al}_2\text{O}_3 \cdot 8\text{SiO}_2$) from Kola apatite deposit and pseudoleicite (mixture of $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$ and $\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) from East-Siberia (Oshurkovo apatite deposit) as admixtures. Their chemical composition is given in Table 1.

TABLE 1 Chemical composition of initial materials, %.

Mineral	P ₂ O ₅	CaO	MgO	R ₂ O ₃	SiO ₂	F	CO ₂
Kovdor apatite	36.5	51.1	2.7	0.7	1.4	1.0	3.4
" "	37.2	52.7	1.5	0.3	0.4	1.2	4.3
Kola apatite	38.8	51.4	<0.1	1.6	3.5	3.3	-

	Na ₂ O	K ₂ O	MgO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂
Glauconite (G)	0.1	8.9	4.3	20.3	10.7	51.1
Nepheline (N)	11.4	6.3	0.2	3.3	22.2	54.3
Pseudoleicite (P)	0.4	15.0	0.3	1.1	21.5	55.7

The ground mixtures of the initial materials with various quantities of aluminosilicate and H₃PO₄ added (up to 10 % and 5 % respectively to the mass of apatite) were calcinated during 1 - 3 h at 1350-1400°C in an electrical tube kiln by passing through air containing up to 20 % water vapour, then rapidly cooled in air. The products availability to plants was estimated by the solubility in 2 % citric acid solution under standard conditions. Chemical, thermal, IR and x-ray methods of analysis were used.

The results of the experiments show that the solubility of the products depends on the choice and quantity of the admixtures as well as on the temperature and duration of heating. Some characteristics of the heated mixtures on the basis of Kovdor apatite are presented in Table 2. As a rule the solubility of the products obtained with glauconite is the lowest, with pseudoleicite - the highest. The solubility of CaO is about the same as P₂O₅, that of MgO to some extent higher, of Fe₂O₃ much lower, of alkali metals - complete. The solubility of P₂O₅ has a relatively good correlation with the degree of defluorination of apatite and with the molar ratio (CaO+MgO) : (P₂O₅+SiO₂) in the products (Fig.). During heating partial volatilization

TABLE 2 Composition and solubility of calcinated samples.

Admixtures, % (to apati- te mass)	Content, %						Solubi- lity of	
	P ₂ O ₅	CaO	MgO	R ₂ O	R ₂ O ₃	SiO ₂	P ₂ O ₅ , % rel.	
-		38.3	55.3	3.0	0.2	0.6	1.7	30.7
- P ₂ O ₅ 2.5		40.0	53.9	2.7	0.5	0.6	1.5	32.8
G6 -		36.5	52.8	3.0	0.4	1.9	5.0	58.6
G6 P ₂ O ₅ 2.5		38.3	51.7	2.8	0.3	1.6	4.6	72.9
N6 "	"	39.2	49.8	1.9	1.1	1.5	6.3	78.0
P6 "	"	38.2	51.5	2.2	0.8	1.5	5.2	85.8

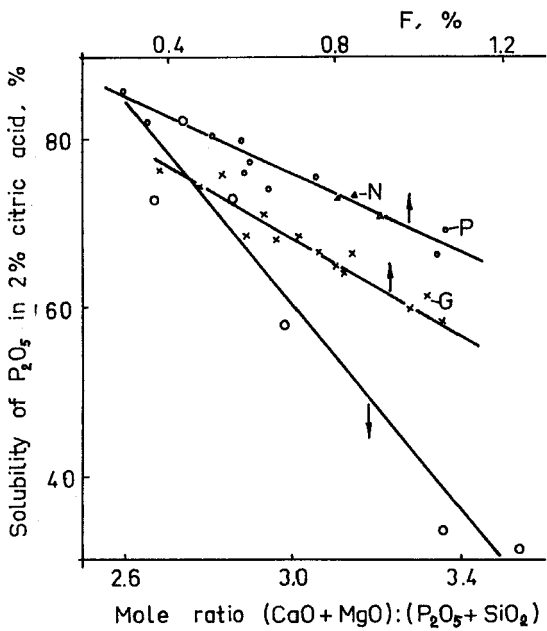


FIGURE 1 Dependence of P₂O₅ solubility on the fluorine content and the mole ratio (CaO+MgO):(P₂O₅+SiO₂) in the mixtures.

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of alkali metals takes place, depending on the completeness of the reactions. Due to the better cristallinity and lower reactivity of Kola apatite the reactions in the mixtures on its basis proceed to a smaller extent, the solubility of the heating products being lower, the loss of R_2O in processing - bigger.

In the crystalline phase of the products α - and β - $Ca_3(PO_4)_2$ (with substitutions), silicophosphates and unreacted apatite were identified. The latter was partly in the form of a more stable A-carbonateapatite formed on heating as a result of relocation of the CO_3^{2-} -ion from the position of PO_4^{3-} -ion to the hexagonal axis of the apatite crystal. The lower solubility of the products obtained with glauconite can be explained by the highest content of Mg and Fe and the lowest content of alkali metals in comparison with other admixtures. Mg and Fe raise essentially the temperature of transition of β - $Ca_3(PO_4)_2$ to more soluble α - $Ca_3(PO_4)_2$ and due to which the latter is formed in a smaller quantity.

Thus, the possibility of getting the available thermophosphates in the sintering process by adding natural alumosilicates to apatite and the dependence of their solubility on the composition of the product have been shown. In comparison with glauconite, nepheline and pseudoleicite proved to be more suitable additives.

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