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COMPOSITION AND PROPERTIES OF THE HEATING PRODUCTS OF THE MIXTURES OF CALCIUM PHOSPHATE AND ALUMINOSILICATES

Abstract. The influence of different compounds (SiO_2, MgO, Al_2O_3, Fe_2O_3) as well as natural aluminosilicates (nepheline, glauconite, pseudoleicite) on the citric acid solubility of the heated mixtures on the bases of calciumphosphates ($CaO:P_2O_5=2.8-3.2$) at 1350—1400 °C has been studied. The products were studied by chemical, X-ray, and IR methods.

In the mixtures with pure reagents the solubility of P_2O_5 is lowered mostly by Mg (by 24.5%), to a lesser extent by Fe (9.4%). Al has practically no influence. The soluble compounds are α- and β-$Ca_3(PO_4)_2$. The insoluble residue contains β-$Ca_3(PO_4)_2$ in which Ca is partly substituted for other cations and also α-SiO_2, α-Al_2O_3, and amorphous iron silicates.

In the mixtures with nepheline and pseudoleicite, the solubility of P_2O_5 is 97—98% when the molar ratios of $SiO_2:P_2O_5>0.21$ and $CaO:P_2O_5=2.9-3.0$. In the mixtures with glauconite, the solubility of P_2O_5 may be as much as 10% lower.

The solubility of phosphorus in the products obtained by hydrothermal treatment of phosphates in 2% citric acid solution does not exceed 30—40% of its total content, which accounts for their insufficiency as fertilizers. Phosphorus is mainly present in the form β-$Ca_3(PO_4)_2$ [1]. For the known solid phase methods used for obtaining thermophosphates as phosphate fertilizers expensive reagents are needed, first of all sodium carbonate. Solubility can be increased also by using natural aluminosilicates (nepheline, glauconite, pseudoleicite), which often accompany phosphates in their deposits [2]. The effect of different aluminosilicates varies essentially due to their different composition (Table 1).

Table 1

Chemical composition of aluminosilicates

Mineral	Na_2O	K_2O	MgO	SiO_2	Fe_2O_3	Al_2O_3
Nepheline (N)	11.4	6.3	0.2	54.3	3.3	22.2
Glauconite (G)	0.1	8.9	4.3	51.1	20.3	10.7
Pseudoleicite (P)	0.4	15.0	0.3	55.1	1.1	21.5

N — $3Na_2O \cdot K_2O \cdot 4Al_2O_3 \cdot 8SiO_2$; G — $K_2O \cdot 4(MgO, FeO, Fe_2O_3, Al_2O_3) \cdot 10SiO_2 \cdot 3H_2O$;
P — $K_2O \cdot Al_2O_3 \cdot 6SiO_2 + K_2O \cdot Al_2O_3 \cdot 2SiO_2$.

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COMPOSITION AND SOLUBILITY OF THE HEATING PRODUCTS OF THE MIXTURES OF CALCIUM PHOSPHATE AND ALUMINOSILICATES

Abstract. The influence of different compounds (SiO₂, MgO, Al₂O₃, Fe₂O₃) as well as natural aluminosilicates (nepheline, glauconite, pseudoleite) on the citric acid solubility of the heated mixtures on the bases of calciumphosphate (CaO:P₂O₅=2.8—3.2) at 1350—1400°C has been studied. The products were studied by chemical, X-ray and IR methods.

The solubility of phosphorus in the precipitate obtained by hydrothermal treatment of phosphorites in 2% citric acid solution does not exceed 30—40% of its total content, which accounts for their insufficiency as fertilizers. Phosphorus also mainly forms the sparingly soluble β-Ca₃(PO₄)₂ [1]. For the sorption of phosphates needed for obtaining thermophosphates also phosphate of hydrogen have been needed, first of all sodium carbonate. Solubility can be increased by using natural aluminosilicates (nepheline, glauconite, pseudoleite), which often accompany phosphate in the deposits [2]. The effect of different aluminosilicates variably essentially due to their different composition (Table 1).

The products and solubility of the main diffraction peaks are presented.

Table 2

Composition and solubility of heating products of the mixture Ca(H₂PO₄)₂·H₂O + CaCO₃ (CaO:P₂O₅=3.2) with admixtures

Admixture, %	Molar ratio $\frac{Me_2O_3+MeO}{P_2O_5+SiO_2}$, MgO, K₂O	Temp., °C	Solubility in 2% citric acid (1:200), % P₂O₅	CaO	MgO Fe₂O₃ Al₂O₃	Insoluble residue %	Insoluble phase	Soluble phase
SiO₂ — 4	3.20	1350	59.8	60.4	—	39.1	OHAp (2.81); α-Ca₃(PO₄)₂ (2.90)	α-Ca₃(PO₄)₂ (2.90)*
		1400	68.4	70.1	—	29.5	OHAp (2.80)	β-Ca₃(PO₄)₂ (2.86)
SiO₂ — 4, MgO — 2	2.57	1350	99.8	99.8	—	2.7	α-SiO₂ (4.00)	β-Ca₃(PO₄)₂ (2.90)
		1400	98.7	98.7	67.0	1.9	α-SiO₂ (4.02)	α-Ca₃(PO₄)₂ (2.90)
SiO₂ — 4, Fe₂O₃ — 2	2.70	1400	76.3	74.9		27.9	β-Ca₃(PO₄)₂ (2.85); α-SiO₂ (4.02)	α-Ca₃(PO₄)₂ (2.88)
	2.50	1350	96.7	95.2	52.1	8.3	β-Ca₃(PO₄)₂ (2.86); α-SiO₂ (4.02)	α-Ca₃(PO₄)₂ (2.90)
		1400	89.3	90.2	50.7	14.3	β-Ca₃(PO₄)₂ (2.87); α-SiO₂ (4.02)	α-Ca₃(PO₄)₂ (2.90)
SiO₂ — 4, Al₂O₃ — 2	2.55	1350	99.2	100	not deter.	5.5	α-SiO₂ (4.04)	β-Ca₃(PO₄)₂ (2.86)
		1400	99.7	98.1		7.6	α-Al₂O₃ (2.08)	α-Ca₃(PO₄)₂ (2.90)

* In parentheses the main diffraction peaks.

It is well known that magnesium, iron, and aluminium raise the temperature of the phase change of β-$Ca_3(PO_4)_2$ to the more soluble α-$Ca_3(PO_4)_2$ from 1180 °C to 1550°, 1450°, and 1250 °C, respectively, hindering the obtaining of assimilable fertilizers [3–5]. At the same time the solubility of calciumsilicophosphates in standard citric acid solution is high [3, 6]. From here arises the need to study the co-effect of the constituent parts of aluminosilicates, particularly as the data presented in literature are contradictory [3–9].

Experimental

In the experiments chemically pure $Ca(H_2PO_4)_2 \cdot H_2O$, $CaCO_3$, $Al(OH)_3$, $MgCO_3$, Fe_2O_3, amorphous SiO_2, and natural aluminosilicates (Table 1) were used. The composition of the initial mixture $Ca(H_2PO_4)_2 \cdot H_2O$ with $CaCO_3$ (molar ratio $CaO:P_2O_5 = R = 2.8$—3.2) and the calcinating temperatures were chosen similar to those used in thermophosphate production. To this mixture the other reagents in amounts 2—20% (mass) were added. The mixtures were calcinated at 1350 °C and 1400 °C during 90 min in an electric oven, then slowly cooled down to room temperature. The heating products were treated with 2% citric acid solution for 30 min, with the ratio of the sample and the solution mass 1:100 or 1:200. The solubility of the mixture components was determined by chemical methods. X-ray and IR methods were used to study the heating products and the insoluble residue in 2% citric acid solution. X-ray diffraction measurements were carried out with a Dron 3M (USSR) instrument (CoKα). IR spectra were taken by a SPECORD IR 75 spectrophotometer using the KBr disc method.

Results and Discussion

Mixtures of pure reagents. According to the data of the experiments the solubility in 2% citric acid solution (sample—solution ratio 1:200) of the initial mixture of $Ca(H_2PO_4)_2 \cdot H_2O$ with $CaCO_3$ ($R = 3.2$), calcinated at 1350 °C and 1400 °C, is 60.9 and 70.5%, respectively (Table 2). The soluble part is α-$Ca_3(PO_4)_2$, the insoluble residue is hydroxyapatite (OHAp).

When 4% of amorphous SiO_2 (molar ratio $SiO_2:P_2O_5 = 0.25$) is added the solubility of the mixture increases to 97.3—98.1%, the solubility of P_2O_5 to 99.8—98.7%. It has been established by X-ray and IR analysis that in the heating products phosphorus is present in the α-$Ca_3(PO_4)_2$ form. The insoluble part consists of α-cristobalite. This is confirmed by IR spectra, where the characteristic absorption bands of Si—O bond appear at 790—810 and 480—510 cm^{-1} (Fig. 1). Partly SiO_2 is in a soluble form (in the composition of the solid solution of α-$Ca_3(PO_4)_2$— α-Ca_2SiO_4)), as the amount of the insoluble residue is smaller than the quantity of SiO_2 in the mixture.

The 2% content of MgO or Fe_2O_3 in the calciumphosphate mixture with SiO_2 lowers the solubility of P_2O_5 to 76.3% or 89.3%, respectively, of its total content. The soluble part of the heated mixture with Fe_2O_3 consists of α- and β-$Ca_3(PO_4)_2$ (with some substitutions). In the mixture with MgO, there is only less soluble β-$Ca_3(PO_4)_2$ present, in which Ca is partly substituted by Mg, as the main diffraction peaks are shifted to lower values (ASTM — 9—169; 20—348). The solubility of Mg is close to that of CaO and P_2O_5, whereas in the mixtures with Fe_2O_3 the solubility of Fe is much lower. This can be explained by the formation of insoluble amorphous iron silicates.
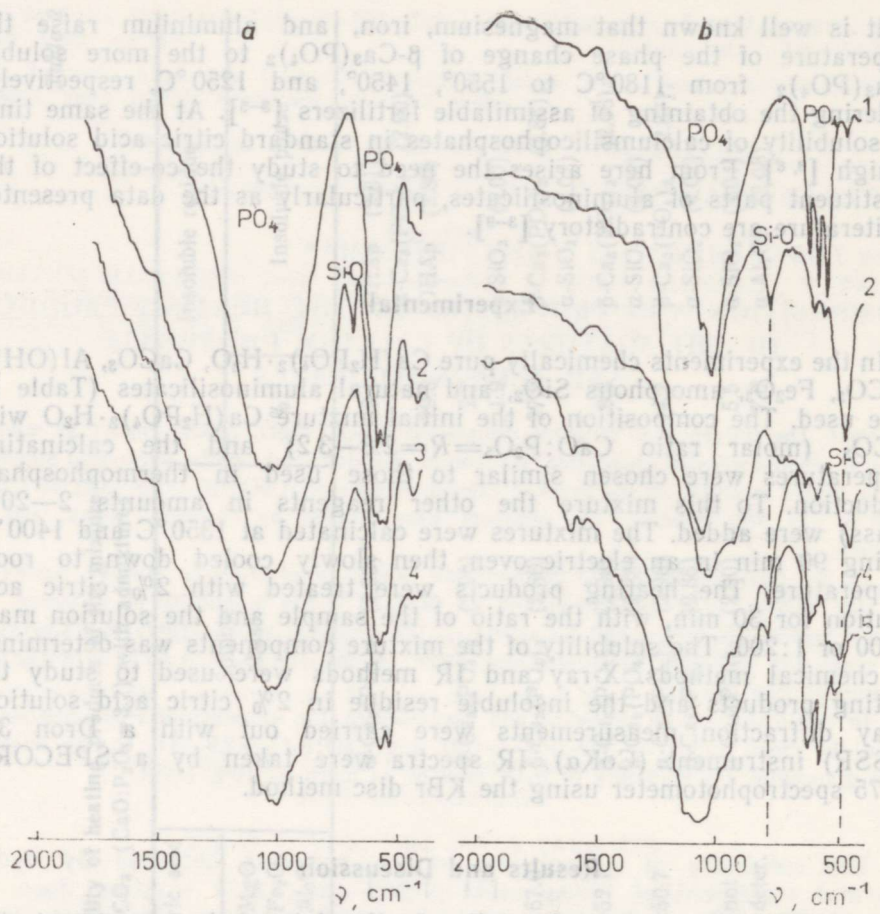
Fig. 1. IR absorption spectra of heating products of the mixture. 1 — $Ca(H_2PO_4)_2 \cdot H_2O$ + +$CaCO_3$ with admixtures; 2 — SiO_2; 3 — SiO_2, Al_2O_3; 4 — SiO_2, Fe_2O_3; 5 — SiO_2, MgO.

a — heating products; b — insoluble residue in 2% citric acid solution.

Aluminium, added as $Al(OH)_3$, does not lower the P_2O_5 solubility in the product. It occurs as α-Al_2O_3 ($d = 2.08$ Å) in the residue.

Therefore, in the mixtures with SiO_2, the solubility of P_2O_5 is lowered mostly by Mg, to a lesser extent by Fe. Al has practically no influence. This corresponds to the decrease in the content of β-$Ca_3(PO_4)_2$ in the products.

Mixtures with aluminosilicates. To the mixtures of $Ca(H_2PO_4)_2 \cdot H_2O$ with $CaCO_3$ ($R = 2.8$—3.2) the aluminosilicates were added in the amount of 5—20% from the mass of the heated calciumphosphate mixture.

The solubility of P_2O_5 of the heating products depends on the conditions of its determination and the molar ratio CaO:P_2O_5 of the mixture (Fig. 2), reaching the maximum value when $R = 2.9$—3.0. In the case of the decrease of the sample—solution ratio from 1:100 to 1:200, the solubility of P_2O_5 increases as the result of the increase in the β-$Ca_3(PO_4)_2$ solubility.
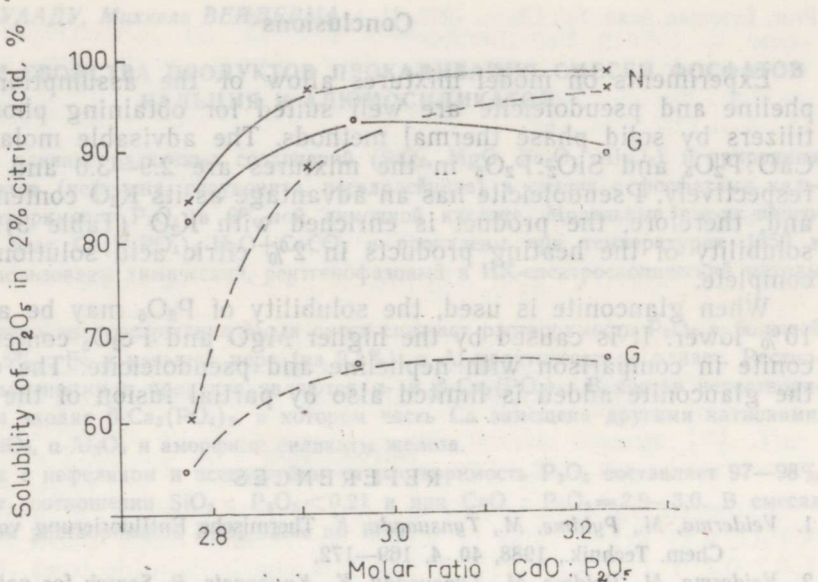
Fig. 2. Dependence of the solubility of P_2O_5 of heating products of the mixture $Ca(H_2PO_4)_2 \cdot H_2O + CaCO_3$ in 2% citric acid with glauconite (G) and nepheline (N) on the molar ratio of $CaO:P_2O_5$. Heating temperature 1350 °C, time 90 min. Sample — solution mass ratio 1:100 (broken line) and 1:200 (solid line).

In the mixtures with glauconite the solubility of P_2O_5 in 2% citric acid solution (1:200) does not rise above 93.2%. When the content of SiO_2 is more than 5%, the amount of the liquid phase increases to the extent of disturbing the solid phase process. The insoluble residue consists of OHAp and $\beta\text{-}Ca_3(PO_4)_2$, in which a part of Ca is replaced by Mg.

The solubility of P_2O_5 is practically complete in the mixtures with nepheline or pseudoleicite, if the molar ratio of $SiO_2:P_2O_5 > 0.21$ (Table 3). The soluble compounds of the heating products are α- and $\beta\text{-}Ca_3(PO_4)_2$, the insoluble residue is $\beta\text{-}Ca_3(PO_4)_2$ with substitutions.

Table 3

Chemical composition and solubility of heating products (1350 °C, 90 min)

Composition, %	$Ca(H_2PO_4)_2 \cdot H_2O + CaCO_3$ ($CaO:P_2O_5 = 3.2$) with					
	Glauconite		Nepheline		Pseudoleicite	
	9%	17%	8%	14%	4%	7%
P_2O_5	39.7	37.5	39.5	37.6	41.7	41.3
CaO	50.8	46.6	50.5	45.9	52.5	51.5
MgO	0.3	0.6	<0.1	<0.1	<0.1	<0.1
Fe_2O_3	2.2	3.8	0.5	0.7	<0.1	<0.1
Al_2O_3	0.7	2.0	2.1	4.6	1.4	2.0
K_2O	0.6	1.4	0.6	1.3	1.0	1.4
Na_2O	<0.1	<0.1	1.3	2.2	<0.1	<0.1
SiO_2	4.8	8.7	4.4	7.7	2.5	3.7
Molar ratio $SiO_2:P_2O_5$	0.29	0.55	0.26	0.49	0.14	0.21
Solubility of P_2O_5 in 2% citric acid (1:200), %	86.5	89.6	97.8	99.7	91.8	96.6

Conclusions

Experiments on model mixtures allow of the assumption that nepheline and pseudoleicite are well suited for obtaining phosphate fertilizers by solid phase thermal methods. The advisable molar ratios of $CaO:P_2O_5$ and $SiO_2:P_2O_5$ in the mixtures are 2.9—3.0 and 0.21—0.25, respectively. Pseudoleicite has an advantage as its K_2O content is higher and, therefore, the product is enriched with K_2O (Table 3). Then the solubility of the heating products in 2% citric acid solution is almost complete.

When glauconite is used, the solubility of P_2O_5 may be as much as 10% lower. It is caused by the higher MgO and Fe_2O_3 content in glauconite in comparison with nepheline and pseudoleicite. The quantity of the glauconite added is limited also by partial fusion of the mixture.

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Kaia TÕNSUAADU, Mihkel VEIDERMA

KALTSIUMFOSFAADI JA ALUMOSILIKAATIDE SEGUDE KUUMUTUSPRODUKTIDE KOOSTIS JA OMADUSED

Et uurida kaltsiumfosfaadi ja alumosilikaatide segudes eri elementide mõju fosfori lahustuvusele 2-protsendilises sidrunhappe lahuses, valmistati mudelsegud $Ca(H_2PO_4)_2 \cdot H_2O$ ja $CaCO_3$ baasil. Segudele lisati SiO_2, MgO, Fe_2O_3, Al_2O_3 või looduslikke alumosilikaate (nefeliini, glaukoniiti, pseudoleutsiiti) ning kuumutati neid temperatuuril 1350° ja 1400 °C. Produkte analüüsiti keemiliste, röntgen- ja IP-spektroskoopia meetoditega.

Fosfaadi lahustuvust segudes vähendab kõige rohkem Mg (24,5% võrra), vähem Fe (9,4%), Al praktiliselt ei mõju. Lahustuvad ühendid produktis on α- ja $\beta\text{-}Ca_3(PO_4)_2$. Mittelahustuv jääk sisaldab $\beta\text{-}Ca_3(PO_4)_2$, milles osa Ca on asendunud teiste katioonidega, samuti $\alpha\text{-}SiO_2$, $\alpha\text{-}Al_2O_3$ ja amorfset rauasilikaati.

Kaltsiumfosfaadi segudes nefeliini ja pseudoleutsiidiga on P_2O_5 lahustuvus 97—98%, kui $SiO_2:P_2O_5$ moolsuhe on suurem kui 0,21 ja $CaO:P_2O_5 = 2,9-3,0$. Segudes glaukoniidiga on P_2O_5 lahustuvus kuni 10% madalam.

Кайа ТЫНСУААДУ, Михкель ВЕЙДЕРМА

СОСТАВ И СВОЙСТВА ПРОДУКТОВ ПРОКАЛИВАНИЯ СМЕСЕЙ ФОСФАТОВ КАЛЬЦИЯ И АЛЮМОСИЛИКАТОВ

Изучено влияние различных соединений (SiO_2, MgO, Fe_2O_3, Al_2O_3) и природных алюмосиликатов (нефелина, глауконита, псевдолейцита) в смесях с фосфатами кальция на растворимость P_2O_5 в 2%-ной лимонной кислоте. Модельные смеси приготовлены на базе $Ca(H_2PO_4)_2 \cdot H_2O + CaCO_3$ и прокалены при температурах 1350 и 1400 °C. Использованы химический, рентгенофазовый и ИК-спектроскопический методы анализа.

Установлено, что содержание Mg в смеси снижает растворимость P_2O_5 в большей мере (на 24,5%), Fe в меньшей мере (на 9,4%), а Al практически не влияет. Растворимыми соединениями в продукте являются α- и β-$Ca_3(PO_4)_2$. В состав нерастворимого остатка входят β-$Ca_3(PO_4)_2$, в котором часть Ca замещена другими катионами, а также α-SiO_2, α-Al_2O_3 и аморфные силикаты железа.

В смесях с нефелином и псевдолейцитом растворимость P_2O_5 составляет 97—98% при мольном соотношении $SiO_2 : P_2O_5 < 0,21$ и при $CaO : P_2O_5 = 2,9—3,0$. В смесях с глауконитом растворимость P_2O_5 ниже на 10%.