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THE INVESTIGATION OF THE CONDITIONS FOR OBTAINING DOUBLE ZINC-CALCIUM PHOSPHATE

ДОСЛІДЖЕННЯ УМОВ ОДЕРЖАННЯ ПОДВІЙНОГО ЦИНКУ-КАЛЬЦІЮ ФОСФАТУ

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Abstract. *The conditions of the synthesis of zinc-calcium phosphate by two principal different methods was determined. The phosphate with general formula $Zn_2Ca(PO_4)_2 \cdot 2H_2O$ were synthesized. The reliable experimental given about conditions of the obtaining of the zinc-calcium phosphate not polluted by additional phases have been established.*

Key words: *synthesis, double phosphate, conditions of obtaining*

Introduction.

In conditions of intensification of technological processes of the most productions of chemical, machine-building and metallurgical industry to questions anticorrosive protection of metals and equipment is spared emphases. Constantly enlarges the variety an inhibitor of corrosions, anticorrosive pigment, varied metallic and non-metallic coating.

High efficiency as anticorrosive pigment show the phosphates of bivalent metals [1,2]. Moreover phosphates, containing in structure two different cations, render greater inhibitive effect, than the individual salts [2]. In this plan perspective anticorrosive by pigment is a double phosphate of the zinc-calcium of the composition of $Zn_2Ca(PO_4)_2 \cdot 2H_2O$. The information about its syntheses have a preparative nature. The systematic researches of the conditions of the obtaining and chemical nature of the double phosphate of the zinc-calcium not carry out.

Considering that efficiency and quality anticorrosive pigment is dependence from purity of the source phosphate, the target given work – to receive reliable experimental given about condition of the reception of the zinc-calcium phosphate not polluted additive phases.

Experimental.

The study of the conditions of the syntheses of the phosphate of the zinc-calcium conducted two in principal different methods. The first of them provided precipitation of $Zn_2Ca(PO_4)_2 \cdot 2H_2O$ from homogeneous system $CaCl_2$–$ZnCl_2$–$(NH_4)_2HPO_4$–H_2O. The researches conducted the method remaining concentration at 25±1° C, using as source 0.1 mol/l water solutions chloride $CaCl_2$, $ZnCl_2$ and 0.5 mol/l solution precipitating agent – $(NH_4)_2HPO_4$. The total concentration cations Ca^{2+} and Zn^{2+} are formed 0.05 mol/l. The relation to source solution n=P/ΣCa,Zn=0.67, k = Zn/Ca – from 0 to 100 mol.%. The mixture solution $CaCl_2$, $ZnCl_2$ and $(NH_4)_2HPO_4$ at given relation gave to reactionary container simultaneously. The educated sediment

separated from solution, washed water, dried at 70° C and analyzed. In uterine solution defined the remaining concentrations of phosphorus ($C_P^{rem.}$, mol/l), zinc ($C_{Zn}^{rem.}$, mol/l) and calcium ($C_{Ca}^{rem.}$, mol/l), measured of pH.

The base of the second method formed the heterogenic interaction mechanical mixture hydroxocarbonate of zinc (72,71% ZnO) and carbonate calcium (54,51% CaO) with solution of the phosphoric acid (64,15% P_2O_5). To separate series experiment installed the dependency of the composition forming solid phase from pH precipitation, the temperature, concentrations H_3PO_4 and correlations of the zinc and calcium to source carbonates.

Results and its discussion.

The results of the analysis of the solid phases and mother liquor, receiving to system $CaCl_2 – ZnCl_2 – (NH_4)_2HPO_4 – H_2O$ upon different correlation of the zinc and calcium in source solution, are presented in tabl.1.

According to given tabl.1, importance n_1=P/ΣCa,Zn in precipitates received under k=Zn/Ca in the field of 0.50≤k≤10.00, corresponds to accounting for average phosphate. However, only at the composition average phosphate, received under 0.50 ≤k≤1.00, are present two cations simultaneously in the manner of one crystalline phase. Their quantitative contents corresponds to the composition of the phosphate of the zinc-calcium of the formula $Zn_2Ca(PO_4)_2·2H_2O$. The results of chemical, X-ray phases and IR spectroscopic analysis, to received for synthesized double phosphate, are similar to famous for $Zn_2Ca(PO_4)_2·2H_2O$.

Table 1

The characteristic of the solid phase in system $CaCl_2 – ZnCl_2 – (NH_4)_2HPO_4 – H_2O$

k= Zn/Ca, atomic	The chemical composition, wt. %					The phases composition (the results from X-ray phases and IR spectroscopic analysis)
	Ca	Zn	P	n_1	n_1'	
0	23,77	0	18,03	0,98	1,00	$CaHPO_4·2H_2O$
0,10	20,86	6,48	17,57	0,91	0,94	$CaHPO_4·2H_2O$ + + $Zn_2Ca(PO_4)_2·2H_2O$
0,20	18,98	10,39	16,69	0,85	0,87	
0,33	12,98	21,84	16,36	0,80	0,79	$Zn_2Ca(PO_4)_2·2H_2O$ +$CaHPO_4·2H_2O$
0,50	11,18	33,29	15,63	0,64	0,70	$Zn_2Ca(PO_4)_2·2H_2O$ *
0,80	9,63	32,87	15,50	0,67	0,69	
1,00	9,47	33,51	15,45	0,66	0,69	
1,25	5,90	37,40	14,62	0,66	0,69	$Zn_2Ca(PO_4)_2·2H_2O$ + $Zn_3(PO_4)_2·4H_2O$
1,50	0,69	41,89	13,43	0,66	0,69	$Zn_3(PO_4)_2·4H_2O$ + $Zn_2Ca(PO_4)_2·2H_2O$
2,00	0	42,39	13,39	0,67	0,69	$Zn_3(PO_4)_2·4H_2O$

*The design values for $Zn_2Ca(PO_4)_2·2H_2O$, wt. %: Zn – 32.96, Ca – 10.11, P – 15.62, H_2O – 9.08.

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The analysis of the composition of the solid phase, to received interaction H_3PO_4 with mixture hydrocarbonate of zinc and carbonate calcium (75° C, ZnO:CaO = 2:1) under different value pH precipitation, has shown that in interval pH 2.1-2.5 sediment presents itself mixture four crystalline phases: $ZnHPO_4·H_2O$, $Zn_3(PO_4)_2·4H_2O$, $CaHPO_4$ and $Zn_2Ca(PO_4)_2·2H_2O$. The molar correlation $ΣMeO/P_2O_5$ in solid phase,

to received within pH 2.8-3.4, most close corresponds to the design values for average phosphate. The X-ray researches is installed presence in composition setting single crystalline phase, identified as double average phosphate of the zinc-calcium of the composition $Zn_2Ca(PO_4)_2 \cdot 2H_2O$. The temperature of the interaction at interval 50-75° C and concentration of the phosphoric acid within 30-87% practically do not influence upon its composition.

For study of the possibility and conditions of the formation double phosphate zinc-calcium different from $Zn_2Ca(PO_4)_2 \cdot 2H_2O$ composition was organized series experiments in which amount of the zinc and calcium in mixture source carbonate changed at over a wide range.

The results chemical and X-ray phases analysis have shown that only at relation Zn:Ca = 2.00 is formed individual chemical compound – a double phosphate of the composition $Zn_2Ca(PO_4)_2 \cdot 2H_2O$. It is a double salt – a compound the constant chemical composition. Increasing the contents Zn or Ca in mixture of source carbonate brings about precipitation alongside with double phosphate proportional amount admixture – $Zn_3(PO_4)_2 \cdot 4H_2O$ or $CaHPO_4$ (tabl. 2).

Table 2

Dependence of the composition phosphate on the ratio source reagents (75°C, pH 3.1, H_3PO_4 – 43% P_2O_5)

Composition of carbonates, Zn:Ca, mol.		Composition of the precipitate, wt %				$\frac{\Sigma MeO}{P_2O_5}$	The phases composition (the results from X-ray phases and IR spectroscopic analysis)
ZnO	CaO	ZnO	CaO	P_2O_5	H_2O		
10	0	52,29	-	30,99	15,72	3,00	$Zn_3(PO_4)_2 \cdot 4H_2O$
9	1	50,44	3,92	31,17	14,41	3,01	
5	1	44,94	9,76	31,91	13,35	3,00	$Zn_3(PO_4)_2 \cdot 4H_2O$ +
3	1	43,56	12,80	32,60	11,01	3,02	+ $Zn_2Ca(PO_4)_2 \cdot 2H_2O$
2	1	40,04	15,20	35,26	9,46	3,00	$Zn_2Ca(PO_4)_2 \cdot 2H_2O$
1	1	31,00	22,42	37,30	9,22	2,90	$Zn_2Ca(PO_4)_2 \cdot 2H_2O$ +
1	3	11,50	38,99	40,44	9,02	2,63	+ $CaHPO_4$
1	5	8,49	40,67	42,57	8,26	2,41	$CaHPO_4$+
1	9	3,28	40,31	49,26	7,15	2,15	+ $Zn_2Ca(PO_4)_2 \cdot 2H_2O$
0	10	-	41,01	52,48	6,02	2,00	$CaHPO_4$

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Conclusions.

The obtained experimental data indicate that to synthesize pure $Zn_2Ca(PO_4)_2 \cdot 2H_2O$ possessing properties of efficient anticorrosive pigment, is possible by two different methods: interaction of aqueous solutions in the system $CaCl_2$-$ZnCl_2$-$(NH_4)_2HPO_4$-H_2O and heterogeneous interaction of zinc and calcium hydroxycarbonates with phosphoric acid. The dependence of the composition of the solid phase formed on the composition of the starting reagents and deposition conditions is shown. Specific conditions for obtaining double zinc-calcium phosphate of $Zn_2Ca(PO_4)_2 \cdot 2H_2O$ composition were determined. Its chemical nature as a double salt of stable composition is revealed.

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Анотація. *Досліджено склад твердої фази, що утворюється у разі осадження катіонів кальцію і цинку у вигляді середніх фосфатів двома принципово різними методами: взаємодією водних розчинів у системі $CaCl_2 – ZnCl_2 – (NH_4)_2HPO_4 – H_2O$ та гетерогенною взаємодією гідроксокарбонатів цинку і кальцію з фосфатною кислотою. Показано залежність складу твердої фази, що утворюється, від складу вихідних реагентів і умов осадження. Визначено конкретні умови одержання подвійного цинку-кальцію фосфату складу $Zn_2Ca(PO_4)_2·2H_2O$. Розкрито його хімічну природу як подвійної солі сталого складу.*

Ключові слова: *синтез, подвійний фосфат, умови одержання.*

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