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## TECHNOLOGICAL ASPECTS OF ENVIRONMENTALLY FRIENDLY PROCESSES OF DOMESTIC PHOSPHORITES REDUCTION

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**Abstract.** Chemical processes of phosphorites reduction by natural gas have been examined in the presence of sodium sulphate. The exchange of soda fluxing additives for sodium sulfate decreases the reduction process temperature, when such valuable products as phosphorus sulfides are formed, namely  $P_4S_{10}$ . We have shown that such exchange allows to reduce the process power consumption.

**Keywords:** environmentally friendly process, phosphorites reduction, phosphorus production, natural gas, sulfide.

### 1. Introduction

Nowadays phosphorus industry of Ukraine suffers from crisis and recession. The lack of domestic high-quality phosphate crude and considerable decrease in apatite concentrate import encourage scientific research on ways to resolve the problem of phosphorus-containing products obtaining. Phosphorus sulfides are used in many branches of national economy, in particular in defense industry, marches and pesticides production, organic synthesis, *etc.*, but their production in Ukraine is absent. Therefore the development of phosphorus sulfides production from native phosphate crude is an urgent problem.

The above-mentioned problems were partially investigated and resolved by famous scientific schools under the guidance of D. Van Weser (USA), E. Tilo (Germany), S. Volkovych, R. Aziev, N. Postnikov, V. Yershov (Russia), D. Kryklyvyi (Ukraine) and others.

Ratnivske deposit of silicum type phosphotires is one of the thick beds of phosphate crude in Ukraine. Its reserves are 784 millions tons with the average content of  $P_2O_5$  5.47%. But there are lots of silica and potassium

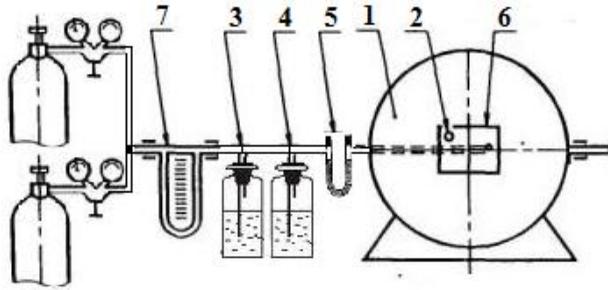
oxide in them. The enriched concentrate contains 19–23% of  $P_2O_5$ .

The aim of the work is to investigate the theoretical and technological aspects of phosphate-containing systems reduction by natural gas in the presence of sodium sulfate to obtain phosphorus sulfides.

### 2. Experimental

The experiments were carried out at the laboratory plant (Fig. 1). An oven (1) was switched on. After reaching the desired temperature the boat loaded by charge (2) was placed into a reactor. The system was inspected for leakproofness. To prevent the formation of explosive mixtures, the system was thoroughly washed by pure nitrogen and gas-reducer was fed. Methane was passed through a washer with a concentrated sulfuric acid (3) to absorb moisture and with potassium hydroxide (4) to absorb acid gases. Then gas is finally dehydrated in calcium-chloride tube (5) and fed to the reaction zone (6). The gas volumetric rate is controlled by a rheometer (7). At the end of the experiment the oven was switched off, the reducer supply was stopped and the system was again washed by pure nitrogen to retard the reaction quickly. The boat with reduced product was moved to the cool part of the reactor for quick cooling. Then it was removed from the reactor and placed into a dessicator for the final cooling. The obtained solid product was analyzed for  $P_2O_5$ , sulfide- and sulfate-ions content. The general amount of phosphorus was determined using the molibdate method [1] and sulfur content – using known methods [2].

Gaseous reaction products were supplied through a system of string-of-spheres absorbers. They were analyzed for  $SO_2$  and  $H_2S$  content by the iodometric method, other gases – by the chromatographic method [3].



**Fig. 1.** Scheme of the experimental plant for phosphate-sulfate crude reduction by natural gas: oven (1); boat with charge (2); washer with concentrated sulfuric acid (3); washer with potassium hydroxide (4); calcium-chloride tube (5); reaction zone (6) and rheometer (7)

To determine a phase composition of the solid product we used X-ray analysis (powder method, DRON-2 diffractometer, Cu-radiation of BSV-27 tube with Ni filter, copper tube plate voltage is 10 kV and current strength is 10 mA) [4].

The phases were identified by the comparative estimation of intensities of the obtained diffractograms which are systematized in Ref. [4-6].

## 3. Results and Discussion

### 3.1. Effect of Different Parameters on Degree of Charge Reduction

The reduction of phosphate-sulfate charge by natural gas is a heterogeneous process. Its rate depends on many parameters: temperature, reaction time, components ratio, *etc.* The surface of reduced charge is also an important factor. The maximum contact of the reacted phases should be provided. It means that first of all it is necessary to determine the process conditions in the solid phase because charge components fusion decreases the contact surface and hence, the rate of the reduction process.

#### 3.1.1. Effect of grain-size distribution

The essential effect on the process efficiency has the reduction ratio of all components of the charge. Thus, it was founded that at 1223 K for 60 min the degree of phosphorus reduction is 97.39 % for the charge with the diameter of no more than 0.25 mm; for the charge with the diameter of 0.5 mm – only 31.84 %. At 1273 K for 60 min the degree of reduction slightly increases. The results concerning grain-size distribution effect are represented in Table 1. The increase of grains size decreases the charge surface and mass exchange. It is followed, in its turn, by the decrease of the charge reduction degree.

#### 3.1.2. Effect of acidity module

It is known that quartzite : phosphorite ratio is defined by the acidity module  $M_a = \text{SiO}_2/\text{CaO}$  [7]. The choice of  $M_a$  is stipulated by the rate and degree of  $\text{P}_2\text{O}_5$  reduction, charge thermal properties *etc.* Its value is within the range of 0.7–3.0 and depends on nature and composition of phosphate and silicon crude. The ratio quartzite (Q): phosphorite (P) in the charge may be calculated according to Eq. (1):

$$\frac{Q}{P} = \frac{M_a [\text{CaO} + \text{MgO}]_p - [\text{SiO}_2 + \text{Al}_2\text{O}_3]_p}{[\text{SiO}_2 + \text{Al}_2\text{O}_3]_q - M_a [\text{CaO} + \text{MgO}]_q} \quad (1)$$

where CaO, MgO,  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  – content of the corresponding components in phosphorite (P) and quartzite (Q).

Acidity module of phosphate charge may determine the reaction proceeding area. During phosphates reduction by gas reduces the thermal stability of phosphate-silicon systems may be controlled by acidity module. Taking into account the importance of this parameter we investigated the effect of acidity module on phosphate charge reduction in the presence of sodium sulfate additives. We used pure phosphate-sulfate systems and temperatures of 1173–1373 K. The results are represented in Table 2.

Table 1

**Dependence of degree of phosphorus reduction ( $\epsilon$ ) from charge on its grain-size distribution (acidity module  $M_a = 3$ ,  $t = 60$  min)**

Grains size, mm	> 1.0	0.5	0.4	0.3	0.25 and less
$\epsilon$ , % at $T = 1223$ K	24.51	31.84	48.63	79.20	97.39
$\epsilon$ , % at $T = 1273$ K	27.1	36.01	52.30	80.11	97.70

Table 2

**Effect of acidity module on degree of phosphorus reduction from phosphate-sulfate charge for 60 min**

$M_a$	1.0	1.5	2.0	2.5	3.0	6
$\epsilon$ , % at $T = 1173$ K	73.4	96.0	96.2	96.5	96.8	95.4
$\epsilon$ , % at $T = 1273$ K	76.8	96.9	97.3	97.4	97.7	97.7
$\epsilon$ , % at $T = 1373$ K	fused	fused	fused	fused	94.1 minor fused	94.0 minor fused

The increase in acidity module has an essential effect on thermal stability of solid-phase products. The residues fusion sharply decreases the degree of phosphorus reduction. Thus, the reduction is more effective at 1173 K compared with that at 1373 K. Fusion and sintering worsen the conditions of gas reducer penetration into phosphate grains. The increase in acidity module from 1 to 6 has a positive effect on the reduction rate and degree of reduction increases by more than 20 %.

The introduction of SiO<sub>2</sub> considerably affects the system physical properties, increases its melting point and favors better diffusion of gas reducer into a solid reagent core allowing to carry out the process in a solid-phase regime.

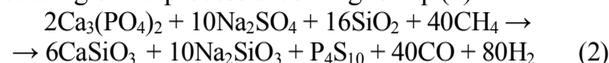
The value of 3.0 was found to be the best acidity module for the investigated system. The absence of intensity peaks of characteristic lines for Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (2.89, 2.62, 3.22) and Na<sub>2</sub>SO<sub>4</sub> (2.78, 3.17, 2.64) confirms the above-mentioned fact and reveals the insignificant effect of acidity module within 1.5–3.0 on the degree of charge reduction. However, the increase of acidity module till 3.0 and higher increases the content of Na<sub>2</sub>O·2CaO·2SiO<sub>2</sub> (4.04, 4.27, 3.80), that is a basis for glass charge.

### 3.1.3. Effect of temperature

The effect of temperature on the degree of phosphate-sulfate charge reduction by natural gas was investigated within 1073–1373 K. In this temperature range *M<sub>a</sub>* is equal to 3 and the reduction proceeds in a solid phase. Process time was 60 min. All experiments were carried out with a reducer amount of 50 % relative to a stoichiometric amount according to Eq. (2). The weight

of charge sample was 1 g. The results are represented in Table 3 and Fig. 2.

Charge reduction at 1073 K proceeds with a sufficient rate. The temperature increase leads to the proceeding of the process according to Eq. (2):



The process is accelerated with the temperature increase and almost complete reduction takes place at 1273 K. Within the temperature range of 1073–1123 K the growth of reduction degree is 0.83 % but within 1223–1273 K this growth is less and was found to be only 0.31 %.

The decline in reduction degree with the temperature increase is probably connected with a process approach to equilibrium state. Minor change of degree with the temperature increase by 50 K indicates possible diffusive area of the process proceeding. The temperature increase above 1323 K does not alter degree of reduction due to the charge fusion and sintering. Charge fusion is conditioned not only by low melting point but formation of eutectic mixtures as well. The obtained products were analyzed using X-ray analysis. The analysis data are in agreement with theoretical calculations and analytic studies.

### 3.1.4. Effect of process time

One of the main factors determining the reduction process intensity is its time during which the maximum yield of the target product is achieved. The experiments were carried out to establish the effect of time on the degree of charge reduction. The results are represented in Table 4 and Fig. 3.

Table 3

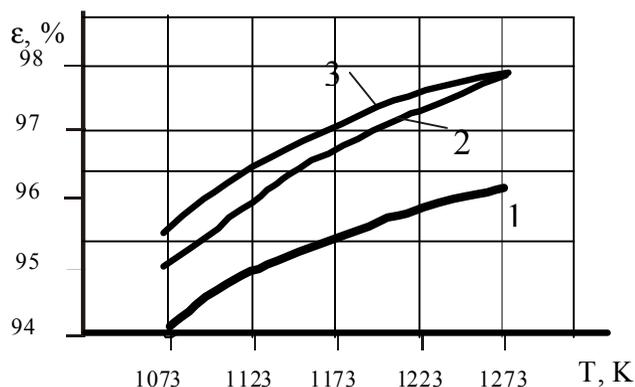
Effect of temperature on degree of phosphorus reduction from the phosphate-sulfate charge (*M<sub>a</sub>* = 3)

Temperature, K		1073	1123	1173	1223	1273	1323	1373
ε, %	τ = 30 min	94.12	95.09	95.47	95.82	96.13	95.46 minor fused	94.04 fused
	τ = 60 min	95.24	96.07	96.80	97.39	97.70	94.96 minor fused	94.1 fused
	τ = 90 min	95.59	96.60	97.02	97.41	97.75	fused	fused

Table 4

Effect of process time on the degree of charge reduction

Time, min		15	30	60	90	120
ε, %	T = 1073 K	46.72	94.12	95.24	95.59	96.03
	T = 1123 K	53.10	95.09	96.07	96.60	96.63
	T = 1173 K	55.21	95.47	96.80	97.02	97.05
	T = 1223 K	56.38	95.82	97.39	97.41	97.45
	T = 1273 K	57.08	96.13	97.71	97.75	97.78



**Fig. 2.** Effect of temperature on degree of charge reduction at different times (min): 30 (1); 60 (2) and 90 (3);  $M_a = 3$

The increase in process time increases the degree of charge reduction. Thus, at 1223 K and process time of 30, 60 and 90 min the values of reduction degree are 95.82, 97.39 and 97.41 %, respectively. If we compare the degree of reduction for 60 and 90 min, it is obvious that the degree increases only by 0.02 %.

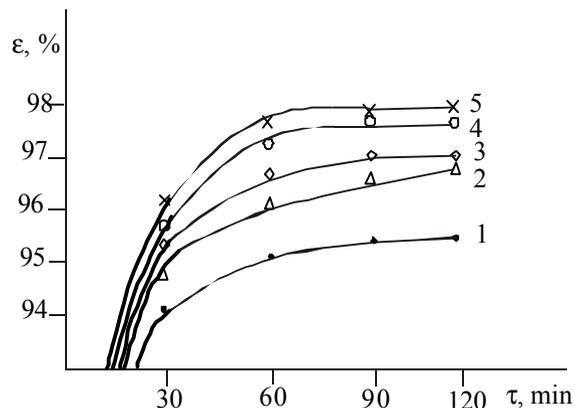
The results of X-ray analysis confirm the above-mentioned. If for 30 min the intensity of peaks typical of  $\text{Ca}_3(\text{PO}_4)_2$  (2.89, 2.62, 3.22) and  $\text{Na}_2\text{SO}_4$  (2.78, 2.64) is still considerable, for 60 min peaks almost disappeared. Moreover, a new crystal phase  $\text{Na}_2\text{O} \cdot \text{CaO} \cdot 2\text{SiO}_2$  (4.04, 4.27, 2.47) appeared with the increase in reduction time. We also observe wide diffuse maximum within  $2\theta$  ranges from 16 to  $30^\circ$  indicating the amorphous phase.

### 3.1.5. Effect of methane consumption

The reducer (methane) consumption affects the reduction of phosphate-sulfate charge the same, as the temperature and process time do. This effect was examined on the basis of Eq. (2). The experiments were carried out with the charge sample of 1 g at 1223 K for 60 min. The results are represented in Table 5.

At methane linear consumption of 4 ml/min (it is approximately 50 % from the results of stoichiometric calculations equal to 490 ml or 8.1 ml/min according to Eq. (2)) the degree of charge reduction is 97.7 %, *i.e.* it is the most effective result. Such low methane consumption and high degree of reduction are caused by participation of hydrogen, which are formed as a result of the reaction (Fig. 4).

With the increase in methane consumption the degree of charge reduction remains constant for definite time and then gradually decreases. At the consumption of 8 ml/min the degree is only 94 %. Thus, the increase of methane supply rate decreases its activity factor and retards the process due to the formation of carbon film on



**Fig. 3.** Effect of process time on degree of charge reduction at different temperatures (K): 1073 (1); 1123 (2); 1173 (3); 1223 (4) and 1273 (5);  $M_a = 3$

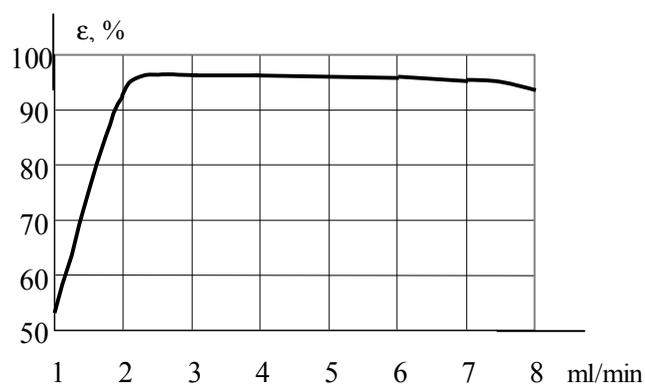
the charge surface hindering the reducer penetration into charge grains.

Table 5

### Dependence of phosphate-sulfate charge degree on reducer consumption

( $T = 1223 \text{ K}$ ,  $t = 60 \text{ min}$ ,  $m = 1 \text{ g}$ )

Methane consumption, ml/min	1	2	3	4	5	6	7	8
ε, %	53.2	92.5	96.3	97.7	97.7	97.0	96.0	94.0



**Fig. 4.** Dependence of degree of reduction on reducer consumption ( $T = 1223 \text{ K}$ ,  $t = 60 \text{ min}$ ,  $m = 1 \text{ g}$ )

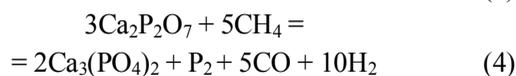
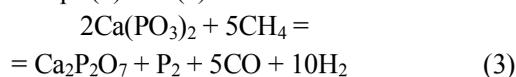
## 3.2. Investigations of High-Temperature Properties of Calcium Phosphate-Silicon Dioxide System

A lot of scientific reports are dedicated to the investigation of the system  $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$  [8-11]. This system is the basis for the production technology of phosphorus and phosphorus products; it is used for the

production of binder materials, *etc.* However there are series of system peculiarities and differences concerning the mechanism of phosphorus formation, as well as peculiarities of phosphorus anhydride acid properties and using the system for other technological processes of inorganic compounds.

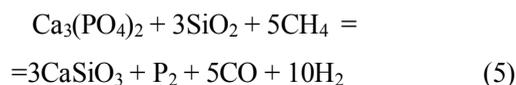
We studied some thermal properties of the system CaO–P<sub>2</sub>O<sub>5</sub>–SiO<sub>2</sub>. In contrast to the traditional technology of phosphorus production, when the high-quality coke is used as a reducer and the process proceeds in the melt, we used natural gas and the process was carried out in the solid-phase regime within the temperature range of 1073–1573 K. The experiment was started from calcium metaphosphate reduction and continued during the reduction process of calcium pyro- and orthophosphate. Materials with high purity were used for the experiment.

To bond calcium oxide formed during phosphorus formation we used silicon dioxide. The results showed that neither calcium dioxide, nor calcium silicate are segregated as a separate phase during calcium metaphosphate reduction in the presence of silicon dioxide. Calcium oxide is released during metaphosphate reduction ( $T = 1173$  K,  $t = 2$  h) and completely used for the increase of phosphorus coordinating saturation. Calcium pyrophosphate is also formed in this system and calcium oxide is used for the increase in thermal and chemical stability of the system. When we reduce calcium pyrophosphate under the presence of silicon dioxide neither calcium oxide nor calcium silicate form separate phases. Calcium oxide is released during pyrophosphate reduction and used only for the increase of phosphorus coordinating saturation, *i.e.* for calcium orthophosphate formation. The studied reduction processes may be represented as Eqs. (3) and (4).



Silicon dioxide is a ballast in these processes because it does not participate in the reduction.

When we reduce Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> by methane, we don't observe the mentioned regularities. Calcium oxide is bounded and calcium metasilicate is obtained in the presence of silicon dioxide. Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> reduction takes place at higher temperatures (1473–1573 K). The process is described by the overall reaction:



It is impossible to distil phosphorus completely during pure Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> reduction [12, 13]. The maximum degree of reduction in such a case is only 50 %. To

estimate the behavior and values of silicon dioxide in the investigated system we studied SiO<sub>2</sub> and CaSiO<sub>3</sub> interaction with phosphorus anhydride at high temperatures. Phosphorus anhydride was distilled in the inert medium in the reactor where SiO<sub>2</sub> and CaSiO<sub>3</sub> samples were loaded. The investigation results are represented in Table 6 and one can see that phosphorus anhydride is actively bounded not only with calcium oxide but with calcium silicate as well.

Phosphorus anhydride displaces silicic acid anhydride from calcium silicate. At 1573 K the bounded amount of P<sub>4</sub>O<sub>10</sub> considerably exceeds the theoretical one that is necessary for tricalcium phosphate formation. At 1573 K even silicon dioxide reacts with phosphorus anhydride and silicophosphate is obtained. The results given in Table 6 do not correspond to the efficiency of P<sub>4</sub>O<sub>10</sub> bounding owing to non-uniform process in the charge volume. The obtained products are fused because of eutectic fusible mixtures formed over the surface.

At 1073 and 1573 K the components ratio Ca:SiO<sub>2</sub>:P<sub>2</sub>O<sub>5</sub> in the reaction products was found to be 0.45:0.45:0.33 and 0.598:0.659:0.216, respectively. Using the calculation method it was established that such ratios corresponds to the formation of 60 % of metaphosphate and 40 % of pyrophosphate at 1073 K and tricalcium phosphate – at 1573 K.

X-ray diffraction analysis confirms the presence of free SiO<sub>2</sub> in the sample at 1573 K. The appearance of silicon dioxide is a result of interaction between phosphorus anhydride and calcium metasilicate. The peak which corresponds to the amorphous substance scattering  $d_{\text{max}} = 4\text{Å}$  and which is typical of amorphous silicophosphate clearly observed at diffractogram. The results of chemical and X-ray analyses allow to assert that phosphorus anhydride is bounded not only with silicon dioxide at high temperatures but may interact with silicate salts and form stable compounds. As it was established previously [14], tricalcium phosphate reduction is retarded in time in the absence of oxide-binding agent. When 50 % of phosphorus is distilled, the reduction is arrested.

We investigated Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> reduction in the presence of calcium oxide. The introduction of CaO into the system (Table 7) also retards the formation of phosphorus.

Phosphorus is reduced from Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> till definite level. If CaO:P<sub>2</sub>O<sub>5</sub> ratio is equal to 6:1, the process is arrested.

All mentioned data show the possible formation of aggregates with a dense pack of atoms resulted in thermal stability of the system (its melting) on the one hand and resistance to reducer penetration into phosphorus in tricalcium phosphate and diffusion of reduced phosphorus out of phosphate system – on the other hand.

Table 6

Molar ratio of the components in the products of P<sub>2</sub>O<sub>5</sub> with SiO<sub>2</sub> and CaSiO<sub>3</sub> interaction

Initial charge composition	Temperature, K	Components molar ratio		
		SiO <sub>2</sub>	CaO	P <sub>2</sub> O <sub>5</sub>
SiO <sub>2</sub>	1473	6.0	–	1.0
CaSiO <sub>3</sub>	1073	1.2	1.2	1.0
CaSiO <sub>3</sub>	1173	1.4	1.4	1.0
CaSiO <sub>3</sub>	1373	1.7	1.7	1.0
CaSiO <sub>3</sub>	1473	2.7	2.7	1.0

Table 7

Effect of CaO on tricalcium phosphate reduced by natural gas (*T* = 1573 K)

Charge composition	Degree of Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> reduction in time, %			
	60 min	120 min	180 min	240 min
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	36.1	43.4	46.5	47.8
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + CaO	22.3	30.2	32.0	33.1
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + 2CaO	9.8	12.3	13.9	15.1
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + 3CaO	3.4	3.8	4.0	4.2

Table 8

Interaction between CaO and Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in reducing and inert media  
(*T* = 1573 K, sample weight is 1 g)

Charge composition	Conditions of thermal treatment		Degree of phosphorus reduction, %	CaO distribution, g		Composition of the obtained product
	Time, min	Medium		Free CaO	Bounded CaO	
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	180	Ar	–	0.0016	0.5398	3CaO·P <sub>2</sub> O <sub>5</sub>
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	60	CH <sub>4</sub>	33	0.0016	0.5403	4.3CaO·P <sub>2</sub> O <sub>5</sub>
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	120	CH <sub>4</sub>	42	0.0106	0.5410	5.1CaO·P <sub>2</sub> O <sub>5</sub>
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	240	CH <sub>4</sub>	50.8	0.0122	0.5322	5.5CaO·P <sub>2</sub> O <sub>5</sub>
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + CaO	180	Ar	–	0.0066	0.5380	3.6CaO·P <sub>2</sub> O <sub>5</sub>
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + 2CaO	180	Ar	–	0.1361	0.1298	4.3CaO·P <sub>2</sub> O <sub>5</sub>
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + 3CaO	3	Ar	–	0.2310	0.1204	4.8CaO·P <sub>2</sub> O <sub>5</sub>

To determine the sizes of reaction aggregates we used the chromatographic method (treatment by liquid nitrogen). The active surface of tricalcium phosphate calcined at 1573 K for 4 h was found to be 2.02 m<sup>2</sup>/g. The calculated atomic volume of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> (weight of 1 g) is 17.936·10<sup>-8</sup> m<sup>3</sup>.

$$r = \frac{3V}{S_0} \quad (6)$$

$$n = \frac{S_0}{4pr^2} \quad (7)$$

where *V* – volume, m<sup>3</sup>; *r* – radius, m; *S*<sub>0</sub> – square of the reaction aggregate, m<sup>2</sup>; *n* – aggregates quantity.

From Eqs. (6) and (7) *r* = 26.638·10<sup>-8</sup>m and *n* = 2.27·10<sup>14</sup> aggregates. The amount of molecules in aggregate  $N = \frac{6.02 \cdot 10^{23}}{310 \cdot 2.27 \cdot 10^{14}} = 8.555 \cdot 10^8$  molecules.

Thus, sufficiently bulky aggregates (reaction centers) containing around 8.555·10<sup>8</sup> molecules of

Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> participate in the process of phosphorus reduction from a phosphate charge.

Phosphorus atom in its excited state has 5 unpaired electrons – 3*s*<sup>1</sup>3*p*<sup>3</sup>3*d*<sup>1</sup> which take place in the formation of chemical bonds and 4 valence *d*-orbitals capable to participate in the formation of additional bonds according to a donor-acceptor mechanism. Phosphorus compounds are generally used with coordinating numbers of 4, 5, 6 and 8; for example calcium tetraphosphate 4CaO·P<sub>2</sub>O<sub>5</sub>, natural phosphates – fluorine apatite Ca<sub>5</sub>F(PO<sub>4</sub>)<sub>3</sub>, hydroxyl apatite Ca<sub>5</sub>OH(PO<sub>4</sub>)<sub>3</sub> and others [15].

On the basis of above-mentioned we forecast that calcium oxide released during reduction of tricalcium phosphate may interact with Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and form more high-coordinating compounds, e.g. 4CaO·P<sub>2</sub>O<sub>5</sub>, 5CaO·P<sub>2</sub>O<sub>5</sub>, 6CaO·P<sub>2</sub>O<sub>5</sub>.

We carried out chemical analysis of the samples obtained after 30–50 % reduction of tricalcium phosphate and samples obtained after sintering of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> with

CaO at 1573 K for 2 h in the inert gas medium. To determine a free calcium oxide the sample was dissolved in water and titrated by 0.1 N solution of acetic acid. The experimental results are represented in Table 8.

Calcium oxide may be bounded with tricalcium phosphate at high temperatures. Moreover, it does not matter if oxide is introduced into the charge composition or it is formed during  $\text{Ca}_3(\text{PO}_4)_2$  reduction. The non-uniform distribution of reagents at charge preparation also affects the process. The formation of high-coordinating products during interaction between  $\text{Ca}_3(\text{PO}_4)_2$  and CaO decreases the oxidative ability of phosphorus(V). The reason is the increase in compounds thermal stability and phosphorus spatial screening by calcium oxide. Therefore it is necessary to destroy such systems by means of deoxidation. For this purpose not only silicon dioxide but  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ , aluminosilicates and other compounds may be used. The main requirement for them is capability to bond calcium oxide at high temperatures.

The capability of phosphorus anhydride to form high-coordinating compounds with the oxides of base nature may be neglected when we use  $\text{P}_2\text{O}_5$  for improvement, for instance, cement clinker. Cement clinking is carried out at 1623–1873 K. Such temperature regime is possible for the formation of high-coordinating phosphate compounds. The additional confirmation is that 2.5 % of  $\text{P}_2\text{O}_5$  improves the cement quality and greater amount – worsens it [15]. To our mind it is connected with retrogradation of cement clinker. Bicalcium and tricalcium silicates interact with tricalcium phosphates and convert into calcium metaphosphate, for which binding properties are not typical.

Taking into account the above-mentioned thermal properties of  $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$  system, namely high reactivity of phosphorus anhydride and calcium phosphates, capability to bind oxides of alkaline, amphoteric and acidic nature, as well as high energy consumption of deoxidation process of  $\text{Ca}_3(\text{PO}_4)_2$  and other phosphates, their decomposition to phosphorus anhydride [16] it should be considered that such systems may be used for localization of high-temperature centers.

On the basis of obtained results we ascertained that calcium phosphates deoxidation by silicon dioxide leading to phosphorus anhydride is improbable. During deoxidation phosphorus anhydride may react with the oxides of alkaline nature, amphoteric oxides and silicon dioxide. At 1573 K phosphorus anhydride may bind with calcium silicate. We also examined the negative effect of  $\text{P}_2\text{O}_5$  high content on the quality of cement clinker. To prevent its retrogradation the additional introduction of lime to the charge composition is necessary. With the aim of phosphorus complete reduction during gas-reducing treatment of phosphate ores the additional additives are needed to be introduced capable to destroy stable high-

coordinating calcium-containing systems. Silicon dioxide, as well as aluminosilicate,  $\text{S}^{2-}$ ,  $\text{Cl}^-$  and other reagents may be used for such purpose.

Taking into account the thermal properties of  $\text{SiO}_2\text{-P}_2\text{O}_5$  system and its ability to bind oxides of alkaline, amphoteric and acidic nature, such system may be recommended for destroying and localization of high-temperature radioactive sources. This system is capable to convert liquid-phase systems into a solid-phase aggregative state, dilute aggressive radioactive centers and bind oxides of heavy metals, including radioactive ones.

## 4. Conclusions

On the basis of calculations of the thermodynamical parameters effect on temperature we approved that exchange of soda fluxing additives for sodium sulfate decreases the reduction process temperature from 1323 to 1223 K, at which valuable products (phosphorus sulfides) are formed,  $\text{P}_4\text{S}_{10}$  first of all. It gives the possibility to unite the production of elemental phosphorus and sulfur into one technological cycle and to reduce the process energy consumption.

The experimental investigations concerning thermal properties of  $\text{CaO-P}_2\text{O}_5\text{-SiO}_2$  system confirm its capability to bind oxides of alkaline, amphoteric and acidic nature, destroy and localize high-temperature radioactive sources, convert liquid-phase systems into the solid-phase aggregative state, dilute aggressive radioactive centers and bind oxides of heavy metals, including radioactive ones.

The effect of temperature on the degree of charge reduction was studied. As a result we may assert: the increase in temperature from 1073 to 1273 K increases the degree of charge reduction; the temperature of 1223 K was found to be the optimum one; at the temperatures above 1273 K the yield of reduction products, namely phosphorus and sulfur decreases.

The investigated method is an environmentally friendly one, no harmful substances are formed and all final products may be used in other technological processes.

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### ДОСЛІДЖЕННЯ ТЕХНОЛОГІЧНИХ АСПЕКТІВ ЕКОЛОГІЧНО БЕЗПЕЧНИХ ПРОЦЕСІВ ВІДНОВЛЕННЯ ВІТЧИЗНЯНИХ ФОСФОРИТІВ

*Анотація.* В статті розглянуто теоретичні та технологічні основи екологічно безпечних процесів відновлення вітчизняних фосфоритів природним газом у присутності сульфату натрію. Встановлено, що заміна содових флюсуючих добавок на сульфат натрію призводить до зниження температури відновлювального процесу з 1323 до 1223 К, при якій утворюються цінні продукти – сульфіди фосфору і, передусім,  $P_4S_{10}$ , що дає можливість знизити енергоємність виробництва.

*Ключові слова:* екологічно безпечний процес, відновлення фосфоритів, технологія отримання фосфору, природний газ, сульфід.