

A.A. Nadtochij, N.M. Velikonskaya

**ANALYSIS OF THE EQUILIBRIUM DISTRIBUTION OF
PHASES OF THE SYSTEM Fe-P-C IN THE
PREPARATION OF PHOSPHORIC FERROALLOYS**

Abstract: A theoretical analysis of the possibility of using phosphorites of domestic deposits as a raw material for the production of ferrophosphorus has been carried out. The equilibrium phase distribution under basicity and temperature variables is considered. The behavior of compounds under reducing conditions is substantiated using programs for thermodynamic modeling.

Keywords: phosphorites, ferroalloys, tricalcium phosphate, reduction processes, basicity, equilibrium composition

Problem formulation.

An increase in the nomenclature and volume of smelting of phosphorus-doped steels increases the requirements for the quality of phosphorous alloying ferroalloys. In Ukraine, ferrophosphorus is not produced, and the demand for it is realized through imports. A study of the mineralogical composition of the phosphorite of Ukraine deposits, carried out after a preliminary analysis of the reduction electrofusion of phosphorite ore and concentrates of its enrichment, showed the possibility of their application to the production of ferrophosphorus. The most promising resource for electrothermal production of phosphorus was considered [1] phosphorites of the Malokamyshevatsky deposit of the Kharkov region (Peremoga site).

The purpose of the article.

Phosphorous ferroalloys are alloys based on iron with a phosphorus content of 15 to 25% [2, 3]. In foundry pig iron, phosphorus improves fluidity. The content of phosphorus from 0.08 to 0.15% enhances the special characteristics of the automatic steel grade A12, corrosion-resistant construction steel 10XHДП, steel grade 08YuP for automotive sheet and others.

The gross composition (% mass) of phosphorite ore from the ore deposit of the "Peremoga" site is shown in Table 1.

It is established [2] that the phosphorus-containing substance in samples of phosphorite ore is represented by a mass of cementing non-metallic minerals (mainly quartz, glauconite, calcite and plagioclase). Energy-dispersive and X-ray phase analyzes made [4] it possible to identify and classify the phosphate material of cement to the francolite mineral.

Table 1

Mineralogical composition of phosphorite ore

P ₂ O ₅ 17,0	Fe ₂ O ₃ 5,05	FeO 0,65	SiO ₂ 31,30	CaO 30,91	MgO 2,45
Al ₂ O ₃ 1,72	MnO 0,30	Na ₂ O 0,42	K ₂ O 0,69	п.п.п. 6,80	F 1,50

Crystallochemical structure of Francolite [5]: Mohs hardness is 5, brittle, density is 3.18 g / cm³. In sedimentary rocks occurs in pelletized grains.

Main material.

In the first approximation, the chemical composition of phosphorite ore can be considered as a ternary system of P₂O₅-CaO-SiO₂, since the content of a mixture of these oxides is more than 80%.

Calculation of the equilibrium in the heterogeneous system P₂O₅ – CaO – SiO₂, carried out using the thermodynamic database "HSC Chemistry 6", without taking into account the formation of solutions and the imperfect behavior of the components, showed the formation of stable high-temperature compounds SiO₂, CaO·SiO₂, 2CaO·SiO₂, 3CaO·2SiO₂, 3CaO·P₂O₅, 2CaO·P₂O₅. In the calculations of the equilibria of the P₂O₅ – CaO – SiO₂ system, the influence of temperature and basicity on the phase distribution was investigated. Initial calculations in the temperature range 1000 - 1800 0C with a 20% P₂O₅ content and basicity equal to 1 are shown in Fig. 1.

Analysis of the data showed that the most stable phosphorus compound is 3CaO·P₂O₅, but at a temperature of ≈ 1400 0C its content decreases with a simultaneous increase in the calcium phosphate content of 2CaO·P₂O₅. Calcium oxide with silicon oxide forms three kinds of double compounds. As the temperature rises, the CaO·SiO₂ content decreases, and the content of 2CaO·SiO₂, 3CaO·2SiO₂ increases.

For a more detailed analysis of the effect of the amount of P₂O₅ in the system on the equilibrium composition of the phases, calculations

were carried out (Fig. 2) at a constant temperature and basicity ($T = 1400\text{ }^{\circ}\text{C}$, $B = 1$).

It was found that an increase in the P_2O_5 content by more than 25% leads to a redistribution of the equilibrium phases: the amount of stable $3\text{CaO}\cdot\text{P}_2\text{O}_5$ decreases and the amount of $2\text{CaO}\cdot\text{P}_2\text{O}_5$ increases, which has a positive effect on the process of recovery.

Investigation of the influence of basicity ($T = 1400\text{ }^{\circ}\text{C}$) on the equilibrium composition of the phases (Fig. 3) made it possible to determine the optimum values of $B = 0,6 - 0,7$.

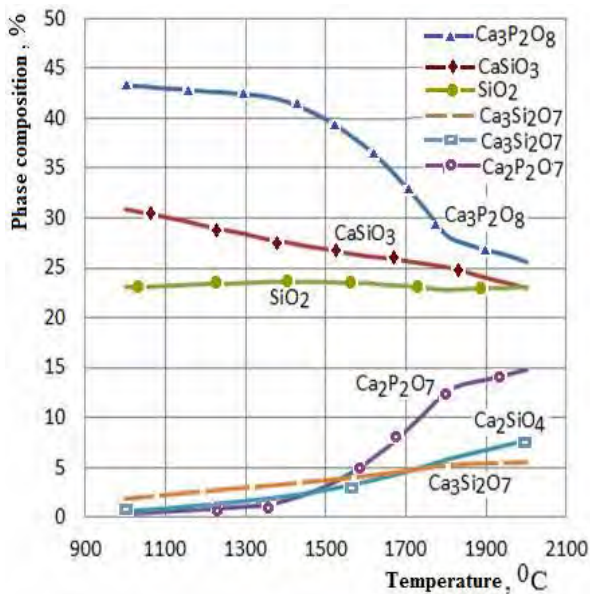


Figure 1 – Equilibrium phase composition of the $\text{P}_2\text{O}_5 - \text{CaO} - \text{SiO}_2$ system in the temperature range $1000 - 2000\text{ }^{\circ}\text{C}$ ($\text{P}_2\text{O}_5 - 20\%$, $B = 1$)

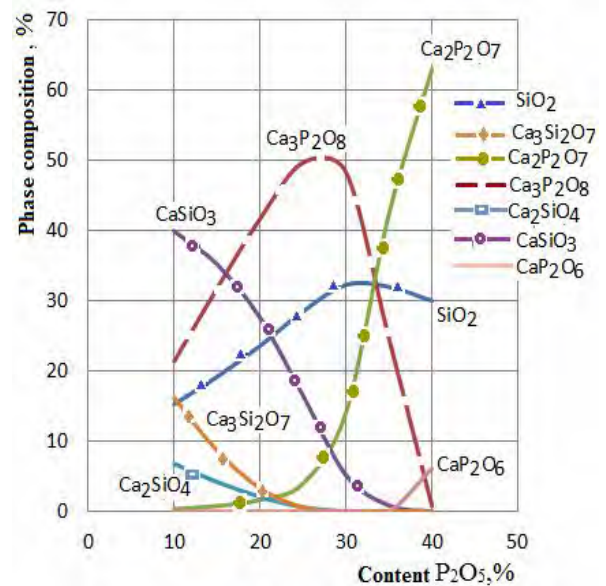


Figure 2 – Equilibrium phase composition of the $\text{P}_2\text{O}_5 - \text{CaO} - \text{SiO}_2$ system as a function of the P_2O_5 content ($T = 1400\text{ }^{\circ}\text{C}$, $B = 1$)

The amount of $2\text{CaO}\cdot\text{P}_2\text{O}_5$ and $\text{CaO}\cdot\text{P}_2\text{O}_5$ decreases, and the amount of tricalcium phosphate, which complicates the recovery process, increases. This is explained by a decrease in the amount of free SiO_2 , which passes into $2\text{CaO}\cdot\text{SiO}_2$, $3\text{CaO}\cdot 2\text{SiO}_2$.

The composition of phosphorites, except P_2O_5 , CaO , SiO_2 , includes Al_2O_3 and MgO . To determine the effect of each component, the $\text{P}_2\text{O}_5 - \text{CaO} - \text{SiO}_2 - \text{Al}_2\text{O}_3$ and $\text{P}_2\text{O}_5 - \text{CaO} - \text{SiO}_2 - \text{Al}_2\text{O}_3 - \text{MgO}$ systems were studied for basicity of 0.7 and 25% P_2O_5 .

When the fourth component of Al_2O_3 is added to the ternary system $\text{P}_2\text{O}_5 - \text{CaO} - \text{SiO}_2$, a complex compound of the composition $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{SiO}_2$ is formed (Fig. 4). When 4% Al_2O_3 is added, signifi-

cant amounts of a low durable CaP_2O_6 compound form in the system, and the addition of 8% Al_2O_3 results in the formation of a significant amount of free P_2O_5 oxide. Thus, the introduction of $\text{Al}_2\text{O}_3 > 8\%$ in the system has a positive effect on the recovery of phosphorus.

Addition of up to 3% MgO to the system does not significantly affect the distribution of phases. An insignificant amount of SiO_2 binds to the compound $\text{MgO} \cdot \text{SiO}_2$.

A theoretical variant for the reduction of oxides of a composition similar to that of a charge during the production of ferrophosphorus is considered. The following quantities of charge materials were chosen as the starting materials: 85 kg of phosphorite ($\approx 20\% \text{P}_2\text{O}_5$), 15 kg of quartzite, 10 kg of coke and 39 kg of iron shavings. Thermodynamic calculations were performed in the temperature range 500 – 1500 $^{\circ}\text{C}$, the data are presented in Fig. 5, 6.

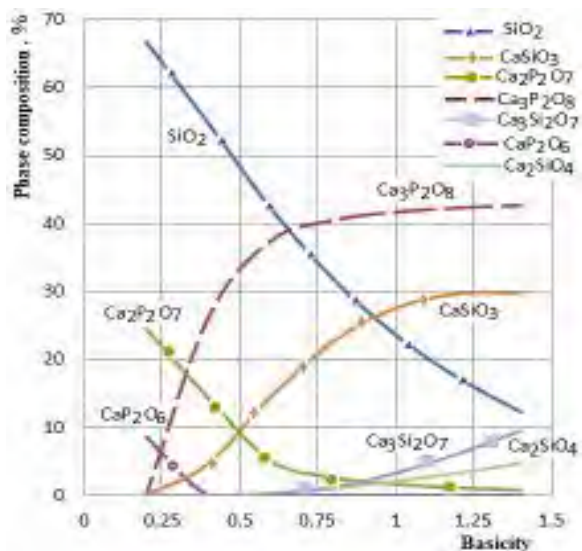


Figure 3 - Equilibrium phase composition of the P_2O_5 - CaO - SiO_2 system, depending on the basicity of the charge ($T = 1400 \text{ }^{\circ}\text{C}$, P_2O_5 -20%)

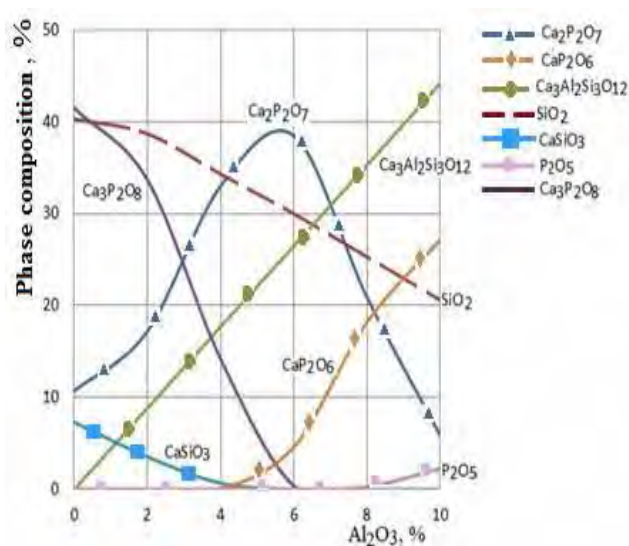


Figure 4 - Equilibrium phase composition of the P_2O_5 - CaO - SiO_2 system as a function of the Al_2O_3 content of the charge ($T = 1400 \text{ }^{\circ}\text{C}$, P_2O_5 - 25%, $B = 0.7$)

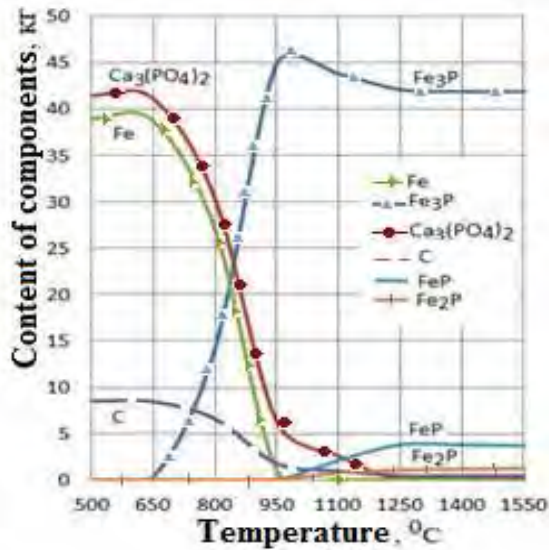


Figure 5 - Equilibrium content of metals components and $\text{Ca}_3(\text{PO}_4)_2$ in the process production of ferro-phosphorus

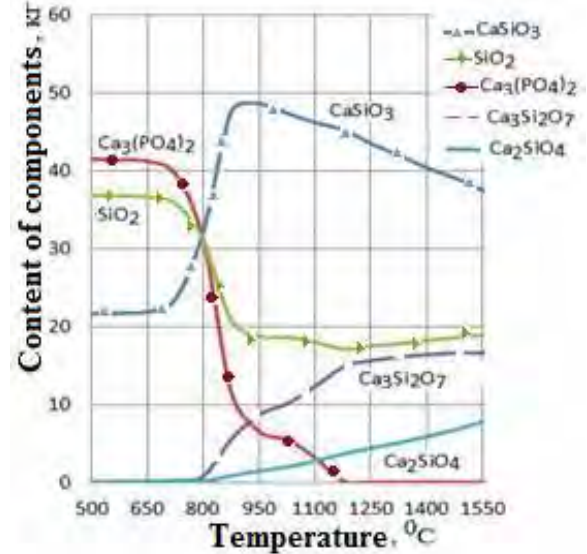


Figure 6 - The equilibrium content of components in the slag system in the production of ferro-phosphorus

Analysis of the calculation shows that all of the phosphorus passes into a durable tricalcium phosphate compound. The carbon reduction of coke begins at 650 °C and ends up to 1250 °C. All the recovered phosphorus dissolves in iron in the form of Fe_3P . At a temperature above 950 °C, the formation of iron phosphides of the composition FeP and Fe_2P is thermodynamically possible. The change in the composition of the gas phase of the ferro-phosphorus smelting process has been studied (Table 2).

Table 2

Theoretical calculation of the change in the composition of the gas phase with an increase in the temperature of the production of ferro-phosphorus

Compound	Temperature, °C					
	500	800	1100	1400	1700	2000
CO	0,03	800	1100	1400	1700	2000
CO ₂	0,01	50,37	85,77	86,84	86,69	86,31
P ₂	$5,2 \cdot 10^{-30}$	11,00	0,27	0,02	0,01	0,02
P	$4,11 \cdot 10^{-28}$	$4,72 \cdot 10^{-18}$	$5,14 \cdot 10^{-04}$	0,1388	0,7187	1,4254
PO	$2,39 \cdot 10^{-22}$	$1,72 \cdot 10^{-17}$	$7,78 \cdot 10^{-08}$	0,0001	0,0021	0,0224
N ₂	99,96	$5,82 \cdot 10^{-13}$	$7,78 \cdot 10^{-06}$	0,0002	0,0008	0,0174

In the gas phase, formation of CO, CO₂, P₂ (gas), P (gas), and PO (gas) is possible. At relatively low temperatures, the reduction of tricalcium phosphate can proceed both with the formation of CO, and with

the formation of CO_2 . But at a temperature of $700 - 750^\circ\text{C}$, the entire CO_2 formed is consumed by the gasification reaction of carbon by the reaction $\text{C} + \text{CO}_2 = 2\text{CO}$.

Significant quantities of phosphorus in the gas phase in the form of P_2 are formed at a temperature of $\sim 1400^\circ\text{C}$ and the content of P_2 increases with increasing temperature. To prevent the fly away of phosphorus to the gas phase, it is necessary to maintain the process temperature no higher than $1300 - 1400^\circ\text{C}$.

As a result of the calculation at 1250°C , the products of reduction melting were installed: 47.8 kg of ferrophosphorus, 81 kg of slag and 18.7 kg of gas. The composition of ferrophosphorus: 17% P, 81.7% Fe, 0.97% C. Thus, theoretical analysis has shown the possibility of using Ukrainian phosphorite as a raw material for obtaining ferrophosphorus with a content of 16 – 17% P according to the accepted in this study the charge.

The results characterize the thermodynamic possibility of reactions between the components of the system, assuming that the system is isolated. In real melting conditions the system is far from equilibrium and the process is carried out in an open system, the interaction proceeds with the losses of matter and energy. Therefore, the obtained indicators are the result of only a thermodynamic calculation, which does not take into account the fly away of the reaction products from the furnace zone, the temperature gradient, the activity of the components, and the kinetics of the process. Thus, the obtained regularities should be considered rather as theoretical boundaries, rather than real quantity.

Conclusions

1. Calculation of the equilibrium in the heterogeneous $\text{P}_2\text{O}_5 - \text{CaO} - \text{SiO}_2$ system showed that an increase in the P_2O_5 content in the system above 25-30% with constant basicity 1 leads to a decrease in the more thermodynamically durable tricalcium phosphate compound and an increase in $2\text{CaO} \cdot \text{P}_2\text{O}_5$.

2. An increase in basicity with a constant amount of phosphorus oxide in the system leads to a decrease in the amount of compounds $2\text{CaO} \cdot \text{P}_2\text{O}_5$ and $\text{CaO} \cdot \text{P}_2\text{O}_5$, and an increase in the quantity of tricalcium phosphate. It is advisable to restore phosphorus from phosphorite at basicity values not exceeding 0,6 – 0,7.

3. Addition to the Al_2O_3 system leads to the appearance of a complex compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2$. With the addition of 4% Al_2O_3 , significant amounts of unstable calcium phosphate CaP_2O_6 appear in the system. The addition of Al_2O_3 above 8% leads to the formation of an appreciable amount of free oxide P_2O_5 . This has a positive effect on the recovery of phosphorus.

4. As a result of the theoretical calculation of the equilibrium for the charge materials: 85 kg phosphorite, 15 kg quartzite, 10 kg coke and 39 kg iron shavings at a temperature of 1250 °C. Obtained: 47.8 kg of ferrophosphorus, 81 kg of slag and 18.7 kg of gas, and the composition of ferrophosphorus, (mass%): 17 P; 81,7 Fe and 0,97 C. Thus, the theoretical analysis showed the possibility of using the Ukrainian phosphorite as a raw material for the production of ferrophosphorus with a phosphorus content of 16 – 17%.

REFERENCES

1. Proydak A.Yu. Investigation of the mineralogical composition of the phosphorous ore of the Malokamyshevat deposit for the smelting of ferrophosphorus / A.Yu. Proydak // Theory and practice of metallurgy. - 2013. - № 5.6. - P. 27-29. (in russia).
2. Girshovich N.G. Handbook of cast iron / N.G. Girshovich. 3rd ed. - L.: Mechanical Engineering, 1978. - 758 p. (in russia)
3. Ershov VA Electrothermy of phosphorus / V.A. Ershov, S.D. Pimenov. - St. Petersburg: Chemistry, 1996. – 248 p. (in russia).
4. Gasik M.I. The nature of the chemical bond of phosphorus in monomineralogic differences and concentrates of manganese ores / NP, VA Gladkikh, M.I. Gasik // Metals. - 1994. - No. 6.- P. 3-11. (in russia).
5. Proydak A.Yu. Experimental study of the process of smelting of ferrophosphorus with the use of phosphorite of the site "Peremoga" / A.Yu. Proydak // Metallurgist, and ore mining. prom-st. - 2012. - №1. - P. 27-29. (in russia).