

Processing of phosphorites with extraction of phosphorus, obtaining calcium carbide and ferroalloy

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Abstract: The article considers the results of studying the thermodynamic computer modeling of the interaction of phosphorite (Karatau basin, Kazakhstan) with carbon and coke performed using the HSC-10 software package and electric smelting of the phosphorite with coke and steel shavings in an arc furnace. The modeling allowed us to determine the equilibrium extraction degrees of phosphorus into gas (P_2 , P_4), silicon into ferroalloy in the form of iron silicides ($FeSi_2$, $FeSi$, Fe_3Si , Fe_5Si_3 , Si) and calcium into CaC_2 . At temperatures above 1500 °C, regardless of the amount of iron, the extraction degree of phosphorus into gas is more 99%. The resulting ferroalloy contains 21.2-23.8% of Si, 1.6-2.8% of Al; the calcium carbide has a capacity of 288-325 dm³/kg. The extraction degree of silicon into the alloy was 89.8%, calcium in CaC_2 – 72.5%, phosphorus into gas – 99.4%. The ferroalloy, formed at the electric smelting of the Chulaktau phosphorite together with coke and steel shavings and containing 24.9-29.8% of Si, is FS25 grade ferrosilicon, and the formed calcium carbide has a capacity of 278-290 dm³/kg and belongs to the third and second grades. The developed technology makes it possible to increase the degree of phosphorites' comprehensive use two times (up to 87.5%).

Keywords: phosphorite, thermodynamic modeling, electrical melting, phosphorus, calcium carbide, ferroalloy

1. Introduction

Kazakhstan is a large phosphorite province, ranking sixth in the world in terms of phosphorite reserves (Alshanov, 2004). According to (Evenchik and, Brodsky, 1987), Kazakhstan phosphorite balance reserves are 2.7 billion tonnes: 1.73 – Karatau basin, 0.97 – Aktobe basin. The average P_2O_5 content in the Karatau phosphorites is 24.5%, in the Aktobe ones – 10%. Both Karatau and Aktobe phosphorites are not used directly to produce orthophosphoric acid (i.e. without their concentration to obtain a concentrate containing $\geq 28\%$ of P_2O_5). The Karatau phosphorites are mainly used to produce phosphorus, and only then phosphoric acid (Weeks and Hettiarachchi, 2019; Wang, et al, 2020; Anouar, et al, 2021;).

Modern electrothermal production of phosphorus from Karatau phosphorites is based on the reduction of tricalcium phosphate with carbon in the presence of silica at 1450-1550 °C according to the reaction (Bogdanov et al, 2009):



A charge consists of phosphorite, quartzite and coke. Its non-metallic components form up to 10-12 tonnes of slag per 1 tonne of phosphorus. The slag is a waste product (46-50% of CaO, 38.6-42.6% of SiO_2 , 3.4-3.7% of MgO, 1.7-2.7% of Fe_2O_3 , 0.6-3.0% of P_2O_5 , 2-3% of CaF_2); it is stored in dumps, occupies land, and worsens the ecology of the region due to the dust formation (Bazhirov et al, 1998). There are some methods for processing phosphorus-containing slags and using them for the production of fertilizers (Hou et al, 2021), brick (Kovkov et al, 2009), silicon dioxide (Bochevskaya et al, 2019), cement (Suleimenov et al, 1980), and concrete products (Khudyakova et al, 2009). However, phosphorus slag has a limited demand in the construction industry due to the fact that it contains P_2O_5 (up to 3%), which forms a poisonous gas – phosphine – in a humid medium (Bazhirov et al, 1998).

It is not possible to reduce the slag formation using the existing electrothermal technology for obtaining phosphorus from phosphorites, since at 1450-1550 °C calcium passes into the slag completely, and silicon by 98-99%. Several methods for processing phosphorites by the thermal method with phosphorus sublimation have been proposed. The use of induction heating makes it possible to reduce the power consumption by 1.5 MWh, P_2O_5 content in the slag to 0.5%, and the dust content of the gases by 8 times (Gorbenko, 1979). When processing phosphorite fines by the plasma method at 2800-3200 K using a combined reducing agent, the productivity of the furnace increases by 7-15%, and the energy consumption decreases by 4 MW h (Kalmykov et al, 1985).

An energy-technological process has been developed for the simultaneous processing of lumpy and fine-grained phosphorite raw materials in a new type apparatus (Fig. 1). Using a furnace with a capacity of 72 MVA can replace 39% of coke and reduce the power consumption by 3 MW h, furnace productivity by 300 kg/h, and cost of 1 tonne of yellow phosphorus by up to 20% (Dontsov, 1979).

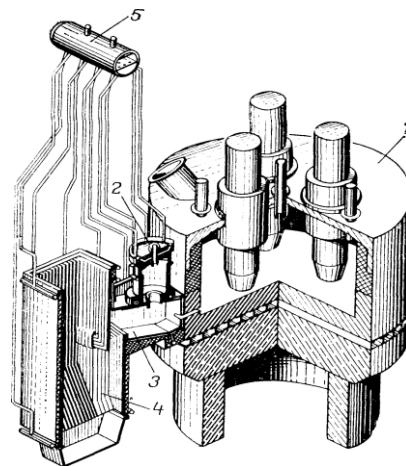
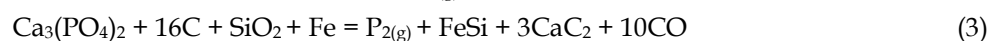


Fig. 1. Energy-technological unit for producing yellow phosphorus (Dontsov, 1979)

1 - electrothermal furnace; 2 - cyclone-type melting device; 3 - melt collector; 4 - radiation chamber; 5 - steam collector

Moscow Institute of Steel and Alloys proposed a new technology for processing phosphorite without the use of electric energy based on the ROMELT reactor (Usachev et al). A charge (phosphorite, coal, flux) is loaded onto the surface of the slag, which is intensively mixed with oxygen-containing blast. There is a liquid-phase reduction of phosphorus, its transition to the gas phase and oxidation to P_2O_5 . In addition to these new processes (Suleimenov et al, 1980; Kovkov et al, 2009; Khudyakova et al, 2009; Bochevskaya et al, 2019; Hou et al, 2021), a method was described for using shungite during the phosphorites' electric smelting, which, due to the presence of carbon and silicon dioxide, makes it possible to replace some of the coke and quartzite (Konevsky et al, 1974).

A reduction-fluxing additive for the charge used for producing phosphorus was proposed (Shevko and Kartbayev, 1997), which contains waste thermal insulation of graphite furnaces as a reducing agent. The method allows replacing scarce coke and part of quartzite with the cheap technical waste. However, the described methods of processing phosphorites by electric smelting, as well as methods for controlling the mode of electrothermal production of phosphorus, which allow improving the technical and economic indicators (Lifson and Yershov, 1994; Pedro, 2014), are characterized by one drawback – the formation of a significant amount of waste slag. The decrease of slag formation during the electric smelting of phosphorites can be achieved by reducing calcium and silicon in a furnace to obtain commercial products. In this regard, we propose the processing of phosphorites with the simultaneous reduction of phosphorus, silica, and calcium and production of a ferroalloy and calcium carbide in an ore-thermal electric furnace with the extraction of phosphorus into the gas phase. The technology is based on the reactions:



The effect of temperature on ΔG° of the reactions is shown in Table 1.

Table 1. Effect of temperature on ΔG° of reactions 2 and 3

Reaction #	Temperature, °C									
	1473	1573	1673	1773	1836	1873	1904	1973	2073	2173
2	955,3	731,6	509,0	287,8	139,5	68,3	0,0	-150	-366,6	-574,8
3	779,7	578,2	385,0	185,6	0,0	-13,0	-74,2	-210,3	-406,4	-594,1

*- ΔG° was calculated using the HSC-10.0 software package (Reactions Equations module) (Roine, 2023).

It can be seen that reaction 2 becomes possible at temperatures above 1904 °C, and reaction 3 – at temperatures above 1836 °C.

This paper presents the results of studying the processing of Chulaktau phosphorite (the Karatau basin) using the proposed method.

2. Materials and methods

The studies included the process' thermodynamic modeling and electric smelting in a single-phase single-electrode furnace.

The thermodynamic modeling was carried out using the HSC-10.0 software package (Roine, 2023) combined with the second-order rotatable designs (Box-Hunter plans) (Akhnazarov, 1985). Thermodynamic system equilibrium parameters with Gibbs minimum energy search are determined by the solution of the mathematical problem of finding the extremum using Lagrange functions and Newton's method of successive approximation. The calculation of the equilibrium degree of the distribution of elements between substances was carried out using an algorithm developed at the M. Auezov South-Kazakhstan university (Shevko et al, 2019).

At the thermodynamic modeling, the CaC_2 content in the technical calcium carbide consisting of CaC_2 and Ca, Al, Fe and Mg oxides – $C_{(\text{CaC}_2)}$ – was determined according to the expression:

$$C_{(\text{CaC}_2)} = \frac{G_{\text{CaC}_2}}{G_{\text{tcc}}} \cdot 100, \% \quad (4)$$

where G_{CaC_2} and G_{tcc} – mass of CaC_2 formed and mass of technical calcium carbide, g, respectively. The calcium carbide capacity (L, dm^3/kg) was determined by the formula (Kozlov and Lavrov 2011):

$$L = \frac{C_{\text{CaC}_2} \cdot 372}{100} \quad (5)$$

where 372 – the volume of acetylene, (dm^3), released during the interaction of 1 kg of chemically pure CaC_2 with water according to the reaction $\text{CaC}_2 + 2\text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{Ca}(\text{OH})_2$.

The number of experiments (N) is determined by the number of independent factors (K):

$$N = 2 \cdot K + 2^K + n_0 \quad (6)$$

where n_0 – the number of experiments the center of the plan, depending on K.

In our case, for two independent factors (temperature, °C; amount of iron, % of the mass of phosphorite), the number of experiments is

$$N = 2 \cdot 2 + 2^2 + 5 = 13 \quad (7)$$

The confidence limit, which is used for determination of the adequacy of the regression equations, in our case is 95%, i.e. the calculation error is no more than 5% (Inkov et al, 2003).

A description of the electric melting installation and the research procedure were published in (Shevko et al, 2023 (a); Shevko et al, 2023 (b)).

The silicon concentration in the alloy $C_{\text{Si}(\text{alloy})}$ was determined using the atomic absorption analysis (AAS-novAA 800), scanning electron microscopy (SEM JSM-6490LV with INCAEnergy energy dispersive microanalysis systems), as well as on the basis of the ferroalloy's density (D, g/cm^3) according to the equation (Shevko et al, 2016):

$$C_{\text{Si}(\text{alloy})} = 3082,79 - 1232,06 \cdot D + 165,738 \cdot D^2 - 7,492 \cdot D^3 \quad (8)$$

The capacity of the calcium carbide produced at the electric smelting of phosphorite in an arc furnace was determined according to the method and on the installation described in (Shevko et al, 2018) In this case the amount of released C_2H_2 is reduced to the following conditions: pressure – 760 mm Hg, temperature – 20 °C. The calcium carbide capacity is calculated according to the formula:

$$L = \frac{(V-B)}{G} \cdot \frac{(P-P_1) \cdot 273}{(273+T) \cdot 760} \quad (9)$$

where P – atmospheric pressure during the analysis, mm Hg; P₁ – water vapour pressure at the analysis temperature, mm Hg; V – volume of released acetylene, ml; G – mass of technical calcium carbide, g; B – volume of water supplied for the decomposition of calcium carbide, ml; T – temperature in the decomposition flask during the analysis, °C.

The determination error according to (Kozlov and Lavrov 2011) is <0.01%.

After determining the capacity, the CaC₂ concentration in the calcium carbide was found using the transformed equation (Inkov et al, 2003).

$$C_{CaC_2} = L \cdot \frac{100}{372} \quad (10)$$

The extraction degree of silicon into the alloy was determined as a ratio of the mass of silicon in the alloy to the mass of silicon in the charge. The extraction degree of calcium into the calcium carbide was determined as a ratio of the mass of calcium in the carbide to the mass of calcium in the charge. The extraction level of phosphorus into the gas phase was calculated in accordance with the expression:

$$\alpha_{P(gas)} = \frac{G_{P(charge)} - (G_{alloy} \cdot C_{P(alloy)} + G_{carb} \cdot C_{P(carb)})}{G_{P(charge)}} \cdot 100 \quad (11)$$

where G_{P(charge)}, G_{alloy}, G_{carb} – mass of the charge, alloy, carbide, respectively, g; C_{P(alloy)}, C_{P(carb)} – the phosphorus content in the alloy and carbide, respectively, fractions of 1.

During the work we used the Chulaktau deposit phosphorite calcined at 1000 °C, containing, wt. %: 51.1 Ca₃(PO₄)₂; 25.59 SiO₂; 12.9 CaO; 1.8 MgO; 1.3 FeO; 0.91 Fe₂O₃; 1.7 Al₂O₃; 0.4 CaSO₄; 0.4 Na₂O; 0.6 K₂O; 0.1 TiO₂; 0.1 MnO; 2.7 CaF₂; 0.5 CO₂; 0.2 H₂O, as well as coke, containing, wt. %: 85.3 C_{solid}, 12.4 ash, 0.4 volatiles, 0.8 S, 1.1 H₂O (the ash contains 2.6% of Fe₂O₃, 2.0% of Al₂O₃, 0.5% of MgO, 1.9% of CaO, 4.91% of SiO₂ and 0.5% others). Carbon steel shavings have the following composition, wt. %: 97.1 Fe; 1.9 C; 0.48 Si; 0.5 Mn; 0.1 others.

When the modeling, the mass of phosphorite was 100 kg, the amount of carbon was equal to 53% of the weight of phosphorite. The amount of iron was varied from 8 to 44% by weight of phosphorite.

3. Results and discussion

The results of the dependences of the equilibrium distribution degrees of silicon in the ferroalloy, calcium in calcium carbide and phosphorus in gas on the process temperature are shown in Fig. 2.

It can be seen that the main substances in the systems in the temperature range of 500-2200 °C are Ca₃(PO₄)₂, CaSiO₃, CaC₂, CaO, CaF₂, Ca_(g), SiO₂, Si, SiO_(g), SiC, Fe₂O₃, Fe, FeSi, P_{2(g)}, P_{4(g)}, Al₂O₃, FeS₂, Mg_(g), Al, MgSiO₃, K₂O*SiO₂, MgO, Na₂SiO₃.

Gaseous phosphorus begins to form in the system in noticeable amounts at temperatures of above 1100 °C. Phosphorus completely passes into gas (as P₂+P₄) at a temperature of ≥ 1500 °C. Phosphides Fe₂P, FeP, FeP₂ are formed in the system in a small amount in the temperature range of 1100-1400 °C. The maximum total extraction degree of phosphorus into the phosphides at 1300 °C is 15.2%. Calcium passes into CaC₂ in the temperature interval of 1800-2200 °C. The maximum transition of calcium into CaC₂ (78.2%) takes place at 2000 °C.

The decrease in the transition degree of calcium into calcium carbide at temperatures of above 2000 °C is explained by its decomposition into carbon and gaseous calcium.

The targeted formation of iron silicides in the system is observed at a temperature of more than 1500°C. Complete Si recovery in the system occurs at 2000°C with the formation of FeSi (mainly) as well as Fe₃Si, Fe₅Si₃, FeSi₂, Si, SiC, Si_{gas}. Silicon maximally (65.55%) passes into the FeSi at 2000°C, and into the elemental state at 1800°C by 12.85%. In fact, silicon is recovered in the system from CaSiO₃. The effect of iron from 8 to 44% on the degree of silicon extraction into the calcium alloy CaC₂, phosphorus into the gas phase is shown in Fig.3. Fig.4 shows the effect of iron on the concentration of silicon in the alloy, CaC₂ in technical-grade calcium carbide and on its gas yield, Fig. 5 shows the effect of iron and temperature on the degree of aluminum extraction into the alloy and the content of this element in it. Fig. 3 shows that an increase in the amount of iron from 8 to 44% in the temperature range of 1500-2200 °C allows increasing α_{Si(alloy)} from 38.70-50.71% to 87.67-92.74%. At the same time, α_{Ca(CaC₂)} decreases from 81.7% to 63.9%. In the temperature interval from 1000 to 1500 °C, an increase in the amount of iron

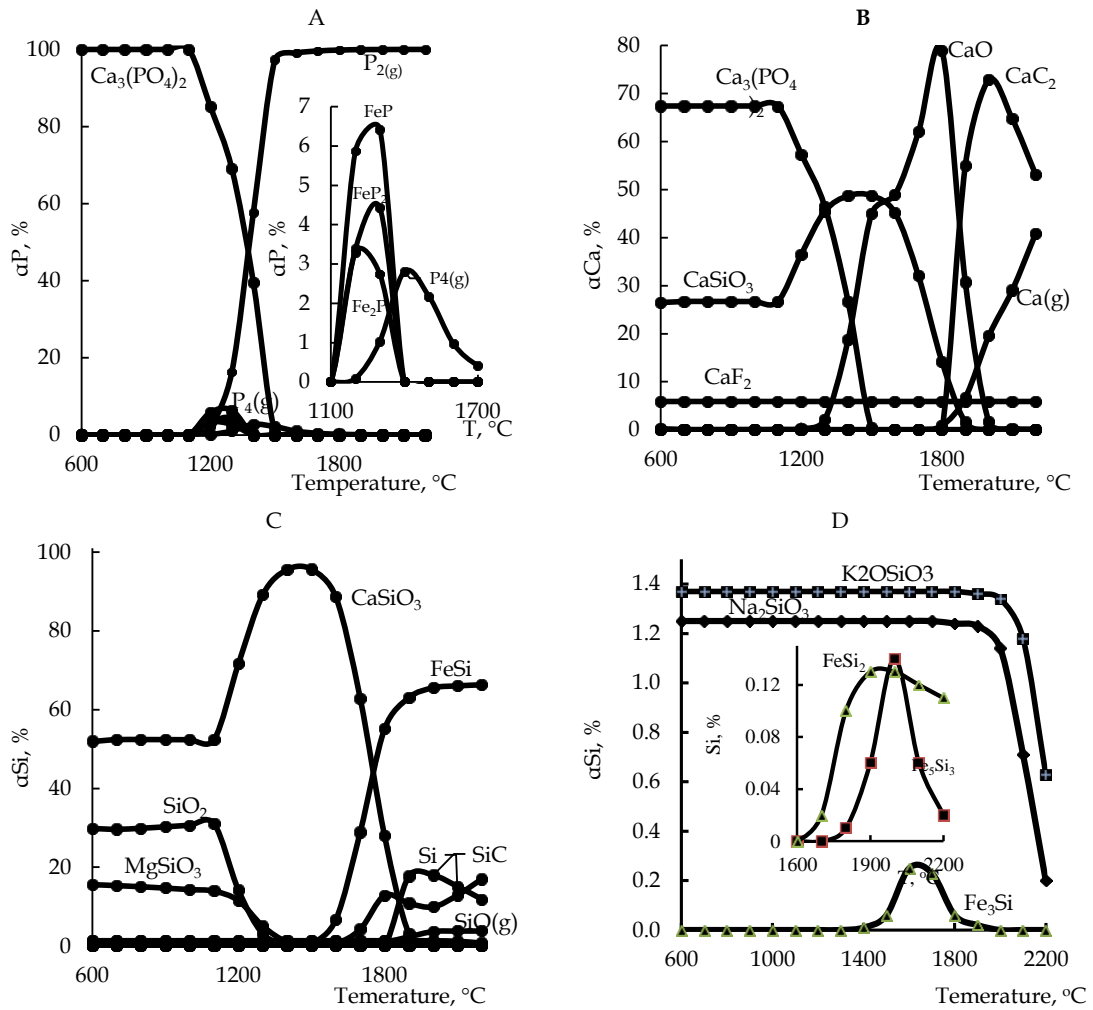


Fig. 2. The effect of temperature and iron on the equilibrium distribution degree of substances containing: phosphorus (a), calcium (b), silicon (c) and iron (d) in the system Chulaktau phosphorite - carbon-26% iron

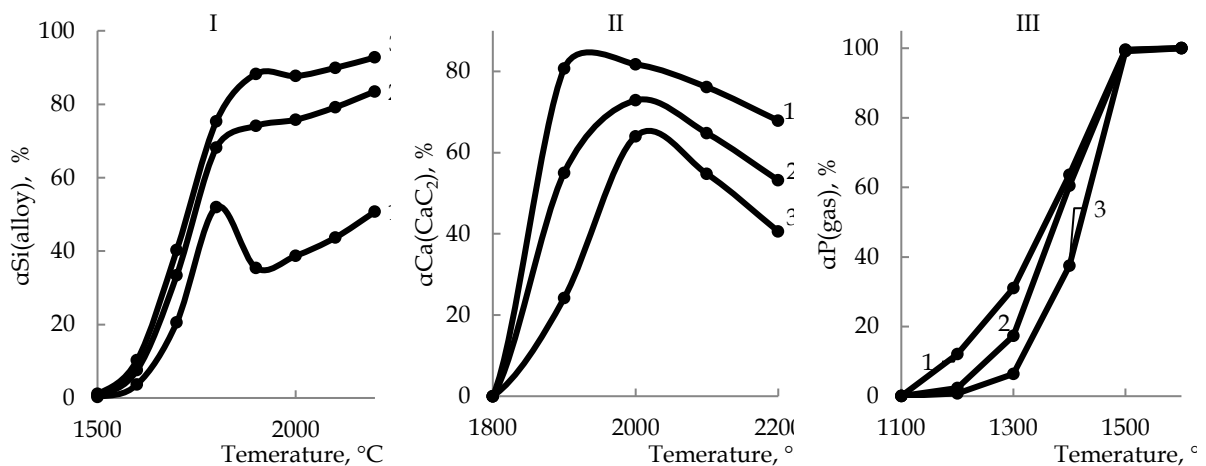


Fig. 3. The effect of temperature and iron on the degree of extraction: of silicon into alloy (I), calcium into calcium carbide (II) and phosphorus into gas (III). Lines are indicated by numbers: 8% iron (1), 26% iron (2), 44% iron (3)

in the charge reduces the extraction degree of phosphorus into gas. However, at 1500 °C all the phosphorus passes into gas. The silicon concentration in the alloy with an increase in the amount of iron in the charge decreases from 37.45% to 15% (1800 °C). Calcium from the phosphorite maximally (86.60%) passes into CaC_2 at 2000 °C in the presence of 8% of iron. An increase in the amount of iron in

the charge reduces $\alpha_{Ca(CaC_2)}$; an increase in iron to 44% lowers the CaC_2 concentration in the carbide to 80% and the calcium carbide capacity to 300 dm³/kg.

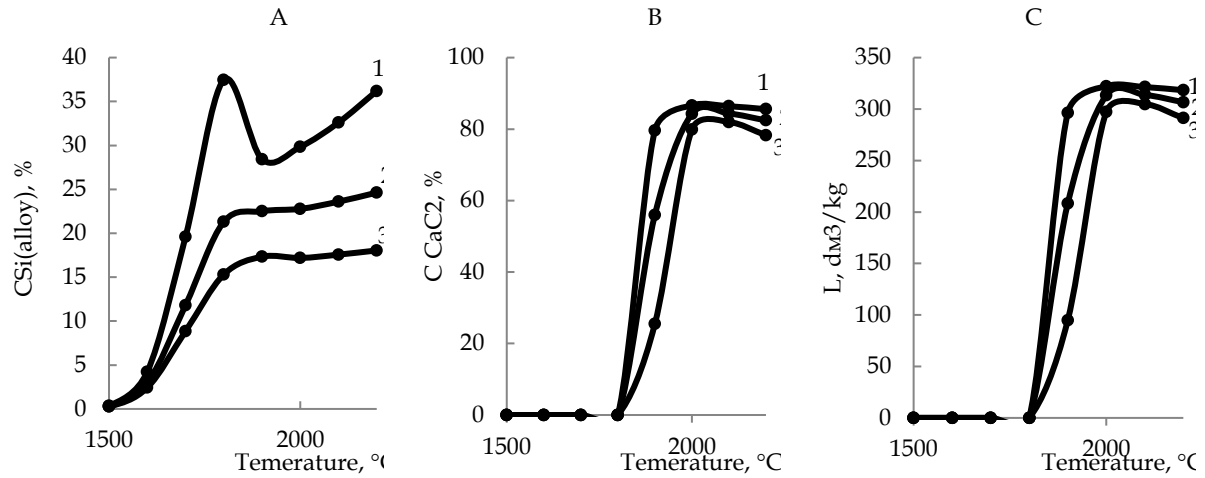
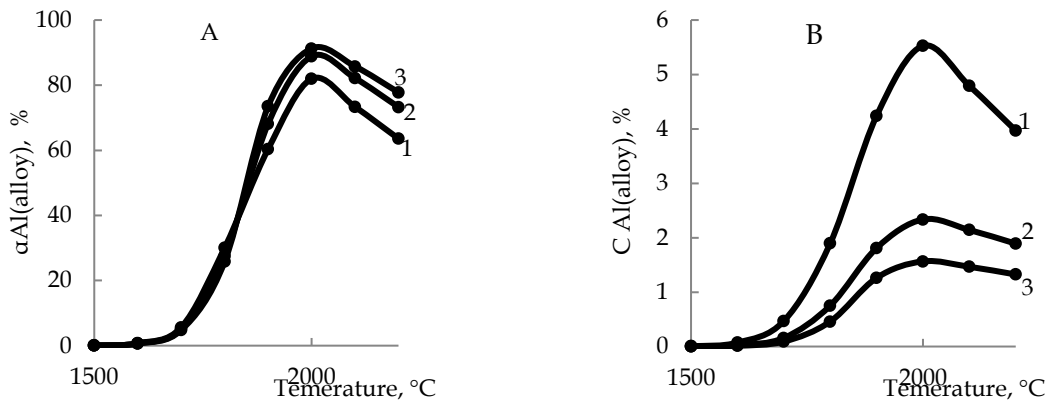


Fig. 4. The effect of temperature and iron on the concentration: of silicon into the alloy (a), CaC_2 into the technical-grade carbide (b), gas yield of technical-grade calcium carbide (c). Lines are indicated by numbers: 8% iron (1), 26% iron (2), 44% iron (3)



Lines are indicated by numbers: 8% iron (1), 26% iron (2), 44% iron (3)

Fig. 5. The effect of temperature and iron on the degree: of aluminum extraction into the alloy (A) and aluminum content into the alloy (B)

Aluminum starts to recover at 1600°C (Fig. 5). An increase in iron from 8 to 44% increases the degree of aluminum recovery and its transition into the alloy at 2000°C to 91.3%. At temperatures of >2000 °C, the extraction of aluminium into the alloy decreases due to its transition into gas. With an increase in the amount of iron in the charge, the concentration of aluminium in the alloy decreases (for example, from 5.4 to 1.6% at 2000 °C).

To determine the optimal temperature and amount of iron, which ensure the maximum extraction of silicon from the phosphorite into the alloy, calcium into calcium carbide and phosphorus into the gas phase and production of commercial products, further studies included planning the experiments using the second-order rotatable designs (Box-Hunter plans), followed by geometric optimization of the technological parameters (Ochkov, 2009). The independent factors in the study were temperature (T , °C) and amount of iron (Fe , % of the phosphorite mass). Taking into account the rather complex dependence of $\alpha_{Si(alloy)}$ on temperature and the amount of iron, two planning matrices were compiled: from 1600 to 1800 °C and from 1900 to 2100 °C.

Based on the data in Tables 2, 3 according to (Inkov et al, 2003; Ochkov, 2009), the following regression equations were obtained:

- at 1600-1800°C

$$\alpha_{Si_{alloy}} = -1227.65 + 5.61 \cdot 10^{-5} \cdot T^2 + 2.48 \cdot 10^{-4} \cdot T \cdot Fe - 1.66 \cdot T - 3.77 \cdot 10^{-4} \cdot Fe^2 - 3.54 \cdot Fe \quad (12)$$

$$Si_{\text{alloy}} = -221.35 + 2.37 \cdot 10^{-6} \cdot T^2 - 3.1 \cdot 10^{-4} \cdot T \cdot Fe + 0.10 \cdot T + 7.1 \cdot 10^{-4} \cdot Fe^2 + 4.60 \cdot Fe \quad (13)$$

• at 1900-2100°C

$$\alpha Si_{\text{alloy}} = 204.97 - 6.67 \cdot 10^{-6} \cdot T^2 - 9.21 \cdot 10^{-5} \cdot T \cdot Fe + 0.22 \cdot T - 3.9 \cdot 10^{-3} \cdot Fe^2 + 5.13 \cdot Fe \quad (14)$$

$$CSi_{\text{alloy}} = 108.68 + 2.57 \cdot T^2 - 2.79 \cdot 10^{-5} \cdot T \cdot Fe - 8.9 \cdot 10^{-3} \cdot T + 2.14 \cdot 10^{-4} \cdot Fe^2 + 0.1 \cdot Fe \quad (15)$$

$$\alpha Ca_{(CaC_2)} = -5264.84 + 6.42 \cdot 10^{-4} \cdot T \cdot Fe - 1.4 \cdot 10^{-4} \cdot T^2 + 5.48 \cdot T - 1.95 \cdot 10^{-4} \cdot Fe^2 - 13.47 \cdot Fe \quad (16)$$

$$L = -21613.35 + 3.18 \cdot 10^{-3} \cdot T \cdot Fe - 5.64 \cdot 10^{-4} \cdot T^2 + 22.26 \cdot T - 1.77 \cdot 10^{-3} \cdot Fe^2 - 64.28 \cdot Fe \quad (17)$$

Using equations 12-17 according to the method (Inkov et al, 2003), we constructed volumetric and planar images of changes in $\alpha Si_{(\text{alloy})}$, $CSi_{(\text{alloy})}$, $\alpha Ca_{(CaC_2)}$, L from temperature and amount of iron, which are shown in Fig. 6-9.

Table 2. Planning matrix in the temperature range 1600-1800°C

№	Variables				$\alpha Si_{(\text{alloy})}, \%$	$CSi_{(\text{alloy})}, \%$
	Coded appearance		Coded appearance			
	X_1	X_2	$T, ^\circ C$	$Fe, \%$		
1	-1	-1	1630	13.2	11.6	5.7
2	+1	-1	1770	13.2	50.3	27.5
3	-1	+1	1630	38.8	17.4	3.9
4	+1	+1	1770	38.8	65.0	14.6
5	+1.414	0	1800	26.0	68.2	21.3
6	-1.414	0	1600	26.0	7.6	3.0
7	0	+1.414	1700	44.0	41.3	8.9
8	0	-1.414	1700	8.0	21.0	19.6
9	0	0	1700	26.0	32.0	12.5
10	0	0	1700	26.0	33.8	12.0
11	0	0	1700	26.0	32.5	11.8
12	0	0	1700	26.0	33.5	11.6
13	0	0	1700	26.0	34.0	11.0

Table 3. Planning matrix in the temperature range 1900-2100°C

№	Variables				$\alpha Si_{(\text{alloy})}, \%$	$CSi_{(\text{alloy})}, \%$	$\alpha Ca_{(CaC_2)}, \%$	$L, \text{ dm}^3/\text{kg}$
	Coded appearance		Coded appearance					
	X_1	X_2	$T, ^\circ C$	$Fe, \%$				
1	-1	-1	1930	13.2	54.1	26.9	81.0	305
2	+1	-1	2070	13.2	56.5	28.4	74.5	318
3	-1	+1	1930	38.8	85.5	18.9	44.5	185
4	+1	+1	2070	38.8	84.6	19.4	61.0	312
5	+1.414	0	2100	26.0	79.2	23.6	64.7	313
6	-1.414	0	1900	26.0	74.1	22.5	55.03	208
7	0	+1.414	2000	44.0	87.7	17.2	63.9	297
8	0	-1.414	2000	8.0	38.7	29.8	82.0	323
9	0	0	2000	26.0	77.0	23.0	72.8	313
10	0	0	2000	26.0	76.8	22.9	73.8	310
11	0	0	2000	26.0	76.5	22.8	73.5	316
12	0	0	2000	26.0	75.3	22.7	74.0	315
13	0	0	2000	26.0	75.0	22.9	71.0	312

Fig. 6 and 7 show that a high (more than 80%) degree of silicon extraction into the alloy is observed in the temperature range of 1900-2000°C in the presence of 27.4-30% iron (darkened area of Fig. 8). The

maximum degree of silicon extraction into the alloy is observed at 2100°C in the presence of 44% iron (dot f in Fig. 7).

Fig. 8 and 9 show that in the system under consideration, the resulting alloy (in terms of silicon content) belongs to ferrosilicon grades FeSi 20 (darkened area) and FeSi 25 (shaded area). It can be seen that ferroalloys are formed in a large range of temperatures and amounts of iron. Therefore, the grade of ferrosilicon should be determined based on the maximum degree of extraction of silicon into the alloy and calcium into the CaC_2 .

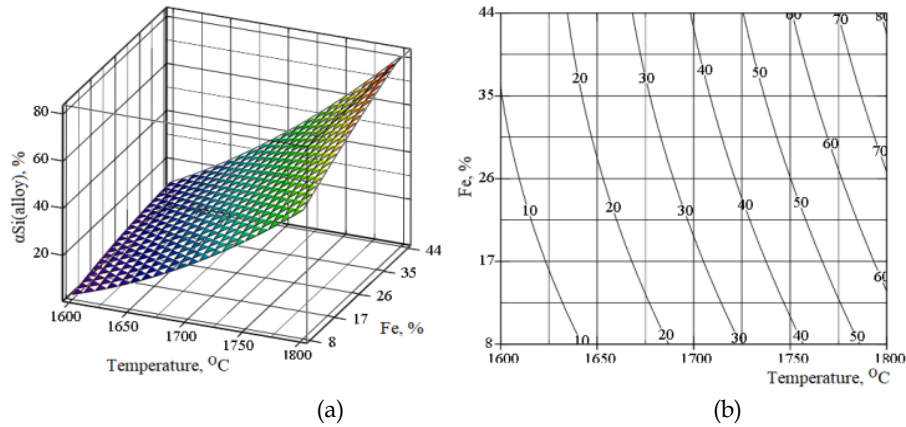


Fig. 6. The effect of temperature and iron on the degree of silicon extraction into the alloy in the temperature range 1600-1800°C. a - Three-dimensional image, b - Linear image

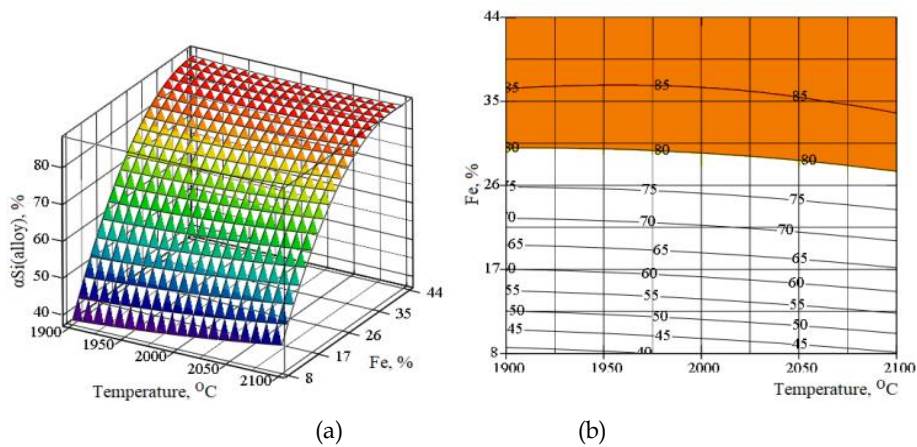


Fig. 7. The effect of temperature and iron on the degree of silicon extraction into the alloy in the temperature range 1900-2100°C. a - Three-dimensional image, b - Linear image

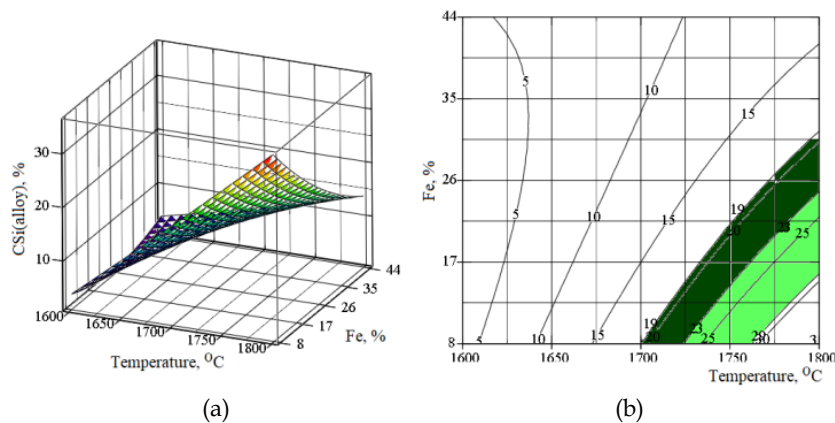


Fig. 8. The effect of temperature and iron on the silicon content in the ferroalloy in the temperature range 1600-1800°C. a - Three-dimensional image, b - Linear image

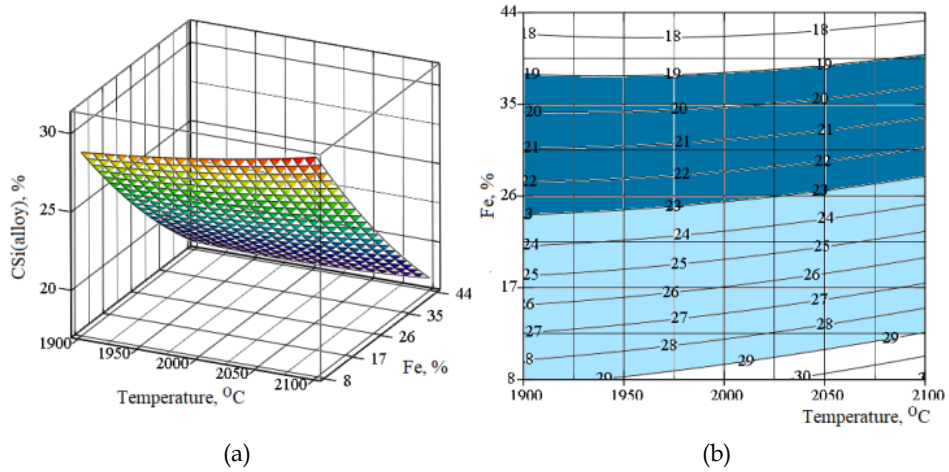


Fig. 9. The effect of temperature and iron on the silicon content in the ferroalloy in the temperature range 1900-2100 $^{\circ}C$. a - Three-dimensional image, b - Linear image

Judging by Fig. 10, the extraction degree of calcium in CaC_2 more than 70% is possible in the temperature range of 1900-2080 $^{\circ}C$ and 8-31% of iron, and more than 80% – at 1900-2040 $^{\circ}C$ and 8-16.9% of iron. The maximum $\alpha_{Ca(CaC_2)}$ (83.6%) is at 8% of iron and temperature of 1975 $^{\circ}C$.

According to (State standard 1460-2013, 2014), high-quality calcium carbide has a capacity of ≥ 230 dm^3/kg . As it follows from Fig. 11, an increase in the process temperature at a constant amount of iron allows increasing in the capacity, and, an increase in the amount of iron at a constant temperature leads to a decrease in the capacity.

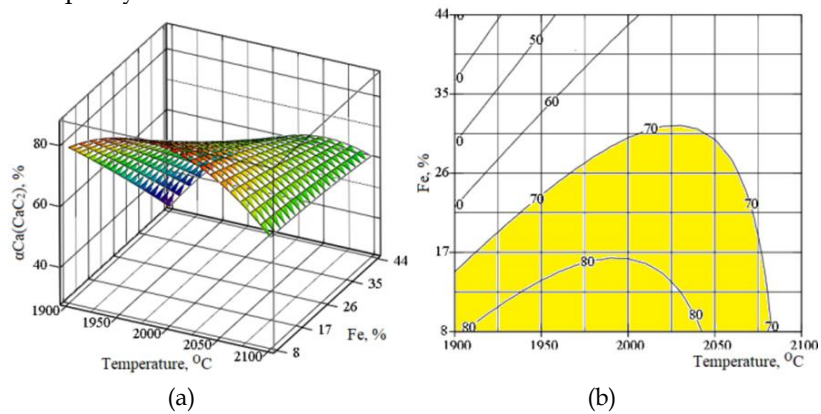


Fig. 10. The effect of temperature and iron on the degree of calcium extraction into carbide. a - Three-dimensional image, b - Linear image

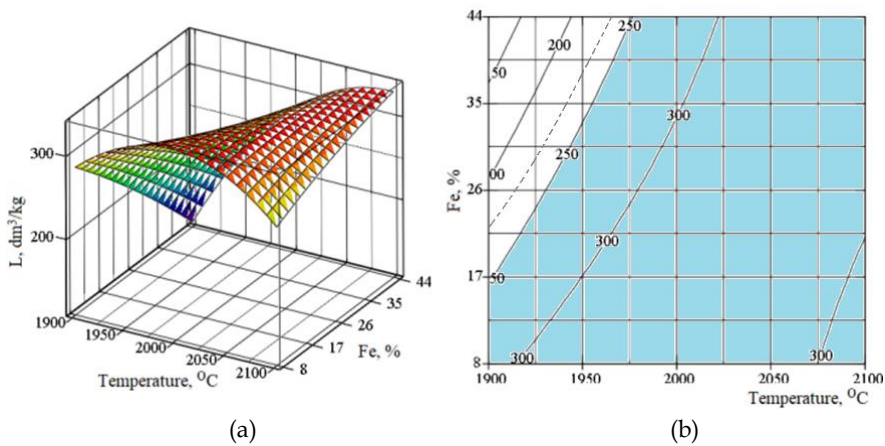


Fig. 11. The effect of temperature and iron on a gas yield of calcium carbide. a - Three-dimensional image, b - Linear image

For determination the optimal conditions for processing Chulaktau phosphorites, it is necessary a joint consideration of the effect of temperature and iron on the technological parameters of extraction and concentration. Fig. 12 shows the combined information about effect of temperature and amount of iron on the technological parameters under the condition of $\alpha\text{Si}_{(\text{alloy})} \geq 75\%$, $\text{CCa}_{(\text{CaC}_2)} \geq 70\%$, $\alpha\text{Al}_{(\text{alloy})} \geq 85\%$, $\text{CSi}_{(\text{alloy})} \geq 2.21\%$. The parameter values in the *abcdnm* region that meets these conditions are shown in Table 4.

Table 4 . Technological parameters at the boundary of the *abcdnm* region of Fig. 12

Point on the Fig.12	Technological parameters							
	T, °C	Fe, %	$\alpha\text{Si}_{(\text{alloy})}$, %	$\text{CSi}_{(\text{alloy})}$, %	$\alpha\text{Ca}_{(\text{CaC}_2)}$, %	$\alpha\text{Al}_{(\text{alloy})}$, %	$\text{CAI}_{(\text{alloy})}$, %	L, dm ³ /kg
a	1963	25.5	75.0	22.8	70.0	84.1	2.7	288
b	1996	29.7	80.2	21.6	70.0	87.7	2.0	304
c	2030	31.5	82.2	21.2	70.0	88.1	1.6	320
d	2050	29.0	80.3	22.1	70.4	87.8	1.8	325
n	2050	28.6	80.0	22.3	70.5	87.2	1.9	325
m	2070	24.4	75.0	23.8	72.3	85.2	2.8	325
f	2050	21.0	70.0	25.0	73.7	82,3	2.4	324
z	1940	21.0	70.0	24.2	71.0	71,4	1.8	279

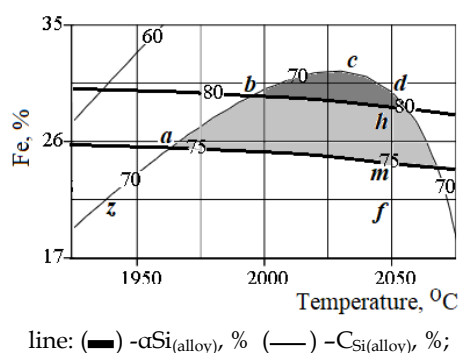


Fig. 12. Combined information about effect of temperature and iron on the technological parameters of interaction in the system phosphorite Chulaktau-carbon-iron

Table 4, Fig. 12 indicate that under the specified conditions, the resulting alloy contains 21-25% Si, and the carbide is characterized by capacity of 297-322 dm³/kg. It should be noted that phosphorus is completely converted into gas in the form of P₂, P₄ and the degree of reduction of aluminum makes up 71-88%. Its content in the alloy made up 1.6-2.8%.

Electric melting of phosphorite from the Karatau deposit was carried out with a charge consisting of: 5 kg of phosphorite (61%), 1.2 kg of steel shavings (1.5%) and 2.0 kg of coke (24%). The degree of silicon extraction into the ferroalloy made up 80.8%. This indicator is 80.5-75.0=5.8% higher than in equilibrium conditions (Fig.12). This is due to the fact that thermodynamic analysis does not take into account the presence of a grate in the furnace, which delays gaseous Si, SiO₂, Si. Therefore, the degree of silicon extraction into the alloy during melting is higher than during thermodynamic modeling.

Photographs of the resulting ferroalloy and calcium carbide are shown in Fig. 13. According to the density of the ferroalloy – 6.32 g/cm³, the alloy, based on (State standard 1415-93, 2011), contains 24.9% of silicon. According to the SEM analysis (Fig. 14), the silicon concentration in the alloy is 27.57%, and judging by the atomic absorption analysis – 29.8%. Thereby, in accordance with the silicon concentration in the alloy of 24.9-29.8% and based on (State standard 1415-93, 2011), the resulting ferroalloy is FeSi25 grade ferrosilicon.

Calcium carbide formed during smelting the phosphorite had a capacity of 270-290 dm³/kg. In terms of its capacity, in accordance with (State standard 1460-2013, 2014), the resulting calcium carbide belongs to the second and first grades. The extraction degree of calcium into calcium carbide was 72.5%.

During the process, phosphorus almost completely (99.4%) passed into the gas phase, and iron into the ferroalloy by 97.6% (the rest of iron almost equally passed into technical carbide and into the gas phase).

The main components of the phosphorite are P_2O_5 , CaO, and SiO_2 and, taking into account the presence of steel shavings' iron in the charge, the degree of comprehensive use of the raw materials is determined by the transition degrees of P, Si, Ca and Fe into the products.

The phosphorus extraction degree during the electric smelting of phosphorites in ore-thermal furnaces is 88%, into ferrophosphorus – 4.5%, iron into ferrophosphorus – 80%. Calcium passes into slag (99%) and into the gas phase (1%); it is not extracted in the products. Silicon passes into ferrophosphorus to a small extent (1.5%).

Therefore, the degree of raw materials' comprehensive use at the electric smelting of phosphorites in the traditional way is (γ , %):

$$\gamma = ((88.0+4.5)+80.0+1.5+0.0)/4=43.5\% \quad (18)$$

and according to the proposed technology:

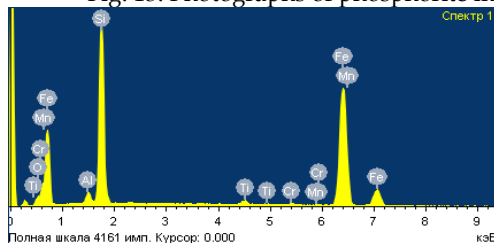
$$\gamma = ((99.5+97.6)+80.8+72.5)/4=87.6\% \quad (19)$$

where 99.5; 97.6; 80.8 and 72.5 – the extraction degree of phosphorus into the gas phase, iron into the ferroalloy, silicon into the ferroalloy and calcium into calcium carbide, respectively.

It can be seen that the proposed technology for processing of phosphorites allows not only to increase the degree of comprehensive use of raw materials by 2 times (by 44%), but it is also slag-free.



Fig. 13. Photographs of phosphorite melting products: (I) ferroalloy, (II) calcium carbide



Element	Weight, %	Element	Weight, %
O	3.22	Cr	0.39
Al	1.86	Mn	0.25
Si	27.57	Fe	65.70
Ti	1.01		

Fig. 14. SEM analysis of the ferroalloy

4. Conclusions

1. The computer thermodynamic modeling of the Chulaktau phosphorite, carbon and iron interaction made it possible to establish that:

- gaseous phosphorus begins to form at a temperature of more than 1100 °C, and its complete transition to gas occurs at 1500 °C; iron phosphides (FeP , FeP_3 , Fe_2P) are formed in a small amount at 1100-1400 °C;
- calcium carbide starts to form at 1800 °C; the maximum calcium carbide formation (83.6%) takes place at 1975 °C and 8% of Fe; then its formation decreases as a result of its decomposition into gaseous calcium and carbon;
- the maximum transition degree of silicon into $FeSi$ (65.55%) occurs at 2000 °C, and into the elemental state – at 1800 °C (12.85%). In fact, silicon in the system is reduced from $CaSiO_3$;
- an increase in the amount of iron in the system leads to an increase in the transition degrees of silicon and aluminium into the alloy and a decrease in the CaC_2 formation, silicon and aluminium concentrations in the alloy and calcium carbide capacity;

- under the optimal conditions (1963-2050 °C, 24.4-31.5% of Fe), the transition degree of silicon into the ferroalloy is 75-80.2%, calcium into CaC₂ – 70.0-72.3%, phosphorus in the gas phase – 99.4%; the resulting ferroalloy contains 21.2-23.8% of Si, 1.6-2.8% of Al and can be attributed to FS25 grade ferrosilicon; formed calcium carbide with a capacity of 288-325 dm³/kg has the highest grade.
2. Experimental electric smelting of the phosphorite with coke and steel shavings makes it possible to produce FS25 grade ferrosilicon (24.9-29.8% of Si) and calcium carbide with a capacity of 270-290 dm³/kg (the 3rd and 2nd grades). The extraction degree of silicon into the alloy in this case is 80.8%, calcium in CaC₂ – 72.5% and phosphorus in the gas – ≥99.5%.
 3. The developed technology allows us to increase the degree of phosphorite's comprehensive use by 2 times (from 43.5 to 87.5%) and it is slag-free.

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