

# ELECTROTHERMAL CO-PRODUCTION OF FERROSILICON, CALCIUM CARBIDE AND GASEOUS PHOSPHORUS FROM THE CHILISAY PHOSPHORITE

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Preliminary Note – Prethodno priopćenje

The article presents the results of studies on the use of the high-silicon phosphorites (51,8 % of  $\text{Ca}_3(\text{PO}_4)_2$ , 25,6 % of  $\text{SiO}_2$ ) for the co-production of ferrosilicon, calcium carbide and gaseous phosphorus. The studies included the electric smelting a charge in an arc furnace and using the second-order rotatable designs. The conditions of producing FeSi45 ferrosilicon (51,2-54,2 % of coke, 12,5-18,4 % of steel shavings) and FeSi25 ferrosilicon (53-58 % of coke, 39,7-40 % of steel shavings) with extraction of 65-67,8 % of silicon into the alloy were determined. The second product of the process is technical calcium carbide with a capacity of 129-167 l/kg, in which from 44,8 to 64,1 % of calcium is extracted. At least 99,3 % of phosphorus during the electric smelting is sublimated.

Keywords: electrothermic process, phosphorite, ferrosilicon, calcium carbide, gaseous phosphorus

## INTRODUCTION

The main silica-containing raw material for producing siliceous ferroalloys is quartzite [1]. So, the production of 1 tonne of FeSi20 ferrosilicon demands 0,37 tonne of standard quartzite, FeSi75 ferrosilicon – 1,93 tonne, ferrosilicomanganese – 0,26-0,33 tonne, FeSi-Cr13 ferrosilico chromium (by the one-stage method) – 0,634 tonne, and FeSiCr48 grade – 1,46 tonne [2]. At the same time, the technology of silicon-containing alloys has recently shown a tendency to use raw materials with a reduced  $\text{SiO}_2$  content. For instance, studies were carried out on the use of shungite rock (35-70 % of  $\text{SiO}_2$ , 20-55 % of C) to produce ferrosilicon, silicomanganese, ferrosilicoaluminium. At the smelting of FeSi25 grade ferrosilicon, the extraction degree of silicon into the alloy did not increase, however, the consumption of quartzite decreased by 3,5-6,9 %, and at the smelting of SiMn17B grade silicomanganese – by 32-39 % [3].

Research was carried out on the use of carbon-quartzite coke containing 70-72 % of  $\text{SiO}_2$  for producing FeSi75 ferrosilicon. In the presence of this raw material, the extraction degree of silicon into the alloy increased from 83 to 88 %, and the energy consumption decreased by 4,5 % [4, 5].

A significant  $\text{SiO}_2$  content in the waste products of carborundum production (30-60 %) and graphite furnaces (20-30 %) served as the basis for their long-term use in the production of silicon-containing ferroalloys [2, 6, 7]. It was shown in [7] that the use of wastes, formed at the

manufacturing graphite products, increases the extraction degree of silicon into the alloy by 2,3 %.

A carbonaceous high ash (up to 65 %) rock of the Ekibastuz basin with the  $\text{SiO}_2$  content in the ash equal to 50-65 % is used as a silicon-containing raw material for the industrial production of ferrosilicoaluminium [8]. The proposed technology makes it possible to obtain FeSi45A10 and FeSi65A20 grades of ferrosilicoaluminium with the extraction of up to 80 % of silicon into the alloy [9].

In addition to natural and technogenic silica-containing raw materials, artificial silica-containing raw materials can also be used to produce silicon-containing ferroalloys. Thus, FeSi20, FeSi25 and FeSi45 grades of ferrosilicon were produced from silica-containing cinder (50-77 % of  $\text{SiO}_2$ ) formed at the chloride sublimation of oxidized copper ores, and FeSi45, FeSi50 and FeSi60 grades of ferrosilicon was smelted using a cake formed after the sulfuric acid leaching of vanadium-containing quartzite [10].

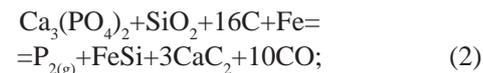
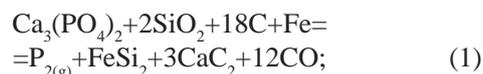
Phosphorites of the Karatau and Aktobe basins containing 10-55 % of  $\text{SiO}_2$ , 10-26 % of  $\text{P}_2\text{O}_5$  and 20-40 % of CaO can become unconventional natural raw materials for producing ferrosilicon [11, 12]. Currently these phosphorites are processed by electric smelting at 1 450-1 500 °C to obtain gaseous phosphorus.

During the electric smelting, 1 tonne of phosphorus gives 10-12 tonnes of waste slag, and  $\text{SiO}_2$  and CaO are completely extracted into the slag. Therefore, the degree of comprehensive use of raw materials is very low. In connection with this, we propose a technology that provides not only the extraction of phosphorus from phosphorites, but also the simultaneous production of ferrosilicon and calcium carbide. The basis of the method is the following reactions:

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Table 1 Planning matrix and experimental results

№	Variables				$\alpha_{Si(alloy)} / \%$	$\alpha_{Ca(CaC_2)} / \%$	$C_{Si(alloy)} / \%$	L / l/kg
	Coded appearance		Coded appearance					
	X1	X2	St.s / %	C / %				
1	-1	-1	14,4	47,8	72,5	53,0	48,8	118
2	+1	-1	35,6	47,8	83,6	38,5	35,2	100
3	-1	+1	14,4	56,2	59,0	70,1	42,0	179
4	+1	+1	35,6	56,2	74,3	54,2	29,3	142
5	+1,414	0	40	25	80,0	38,5	32,3	180
6	-1,414	0	10	25	61,3	63,6	48,4	159
7	0	+1,414	25	58	64,9	66,8	34,6	168
8	0	-1,414	25	46	82,3	43,6	43,2	90
9	0	0	25	52	74,5	53,1	37,4	138
10	0	0	25	52	75,7	52,6	37,9	139
11	0	0	25	52	74,0	53,8	38,6	140
12	0	0	25	52	74,8	52,5	37,7	142
13	0	0	25	52	74,9	52,9	38,0	141



from a thermodynamic point of view (according to  $\Delta G=0$ ), these reactions become possible at temperatures of  $>1\ 702,8$  and  $>1\ 836$  °C, respectively ( $\Delta G^0$  was calculated using the HSC-10.0 software package (Reactions Equations module)) [13].

This article presents the experimental results obtained at the electric smelting of the Chilisay deposit phosphorite (the Aktobe basin) with the purpose of obtaining ferrosilicon, calcium carbide and distillation of phosphorus.

### MATERIALS AND METHODS

The components of the charge used for the electric smelting:

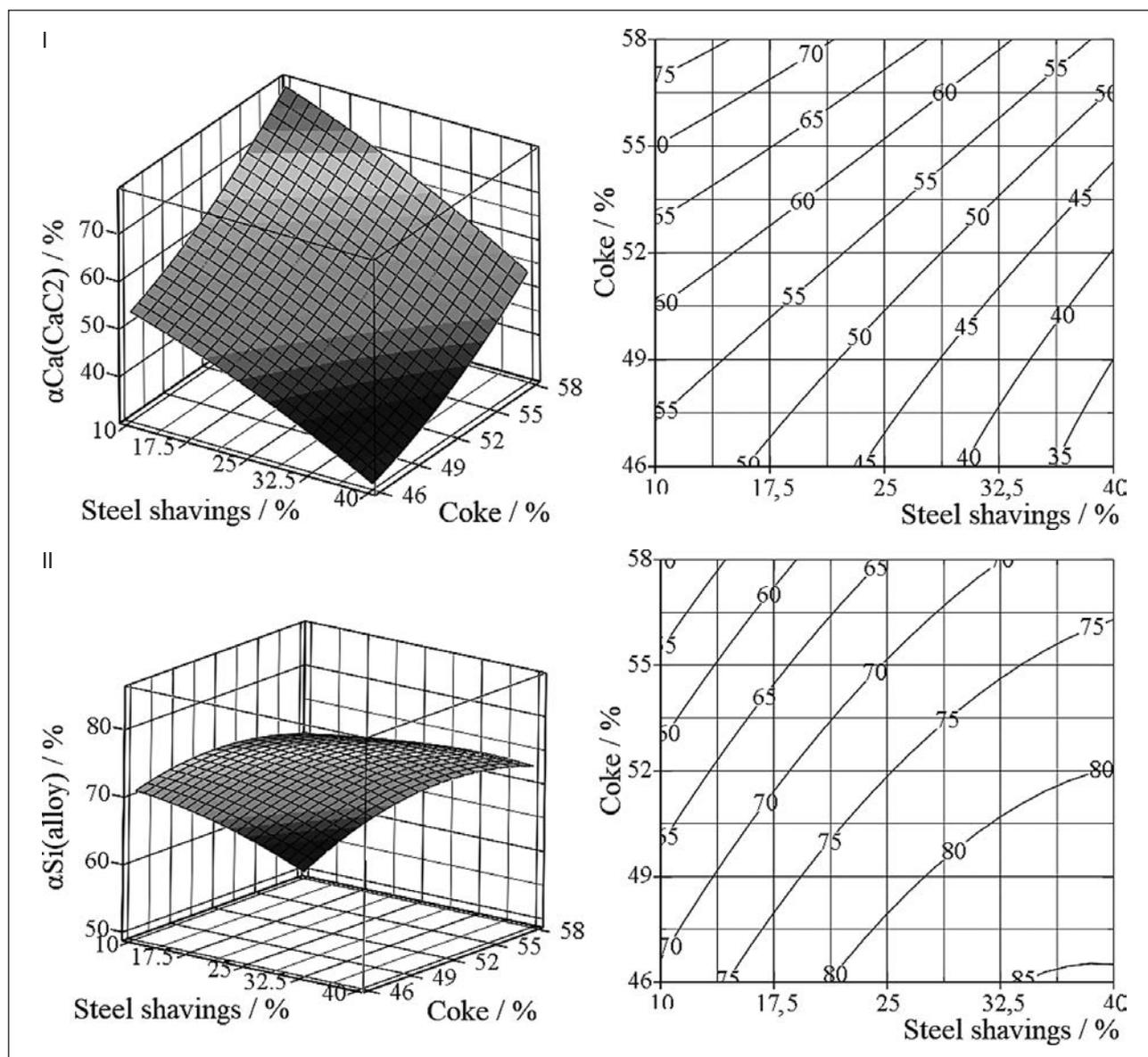


Figure 1 The effect of steel shavings and coke on  $\alpha_{Si(alloy)}$  – (I) %,  $\alpha_{Ca(CaC_2)}$  – (II) %

The phosphorite after calcination at 950 °C contained wt. %: 51,8 Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>; 25,60 SiO<sub>2</sub>; 10,6 CaO; 1,8 MgO; 3,5 Fe<sub>2</sub>O<sub>3</sub>; 1,7 Al<sub>2</sub>O<sub>3</sub>; 0,4 CaSO<sub>4</sub>; 0,4 Na<sub>2</sub>O; 0,6 K<sub>2</sub>O; 0,1 TiO<sub>2</sub>; 0,1 MnO; 2,7 CaF<sub>2</sub>; 0,5 CO<sub>2</sub>; 0,2 H<sub>2</sub>O. The composition of coke, wt %: C-86,0; SiO<sub>2</sub>- 4,9; Fe<sub>2</sub>O<sub>3</sub>- 2,2; CaO -1,5; Al<sub>2</sub>O<sub>3</sub>- 1,8; MgO-0,4; S - 0,8; H<sub>2</sub>O - 1,1; others-1,3. The composition of steel shavings wt. %: Fe-97,6 %, C-1,7 %, Si -0,3 %, Mn -0,2 %, Cr-0,1, others-0,1 %. The composition of quartzite, wt %: SiO<sub>2</sub> - 97; CaO -0,7; Al<sub>2</sub>O<sub>3</sub> - 0,8; Fe<sub>2</sub>O<sub>3</sub>-0,8; H<sub>2</sub>O-0,1; others- 0,3.

The raw materials had a fraction of 0,5-1 cm.

A scheme of the experimental installation, the technique of electric melting and methods for determination of the extraction degrees of silicon into an alloy, calcium into calcium carbide, and phosphorus into the gas phase were published by us in [14,15].

## RESULTS AND DISCUSSION

The studies were carried out by the experiment planning method using the second-order rotatable designs (Box-Hunter plans) [16]. The derivation of regression equations and the construction of graphical images of changing the technological parameters depending on the amount of coke (C / %) and steel shavings (St, %) were implemented according to the techniques [17, 18]. The experiments' planning matrix and results are shown in Table 1.

Based on the data in Tables 1 according to [16], the following regression equations were obtained:

$$\alpha_{\text{Si(alloy)}} = 70,194 + 0,29 \cdot \text{St} + 1,14 \cdot \text{C} - 17,87 \cdot 10^{-4} \cdot \text{St}^2 - 30,27 \cdot 10^{-4} \cdot \text{C}^2 + 23,58 \cdot \text{St} \cdot \text{C} \quad (3)$$

$$\alpha_{\text{Ca(CaC}_2\text{)}} = 158,16 - 3,1 \cdot 10^{-3} \cdot \text{St} - 5,61 \cdot \text{C} - 6,74 \cdot 10^{-4} \cdot \text{St}^2 + 7,4 \cdot 10^{-3} \cdot \text{C}^2 - 7,86 \cdot 10^{-4} \cdot \text{St} \cdot \text{C}; \quad (4)$$

$$C_{\text{Si(alloy)}} = 149,08 - 1,29 \cdot \text{St} - 2,63 \cdot \text{C} + 9,12 \cdot 10^{-4} \cdot \text{St}^2 + 1,70 \cdot 10^{-3} \cdot \text{C}^2 + 5,05 \cdot 10^{-4} \cdot \text{St} \cdot \text{C}; \quad (5)$$

$$L_{\text{Si}} = 1120,92 + 4,30 \cdot \text{St} + 40,70 \cdot \text{C} + 1,11 \cdot 10^{-4} \cdot \text{St}^2 - 0,30 \cdot \text{C}^2 - 0,10 \cdot \text{St} \cdot \text{C}. \quad (6)$$

Then, the volumetric and planar images of changes in the process parameters were constructed. For example, the  $\alpha_{\text{Si(alloy)}}$  and  $\alpha_{\text{Ca(CaC}_2\text{)}}$  planar images are shown in Figure 1.

Judging by Figure 1,  $\alpha_{\text{Si(alloy)}}$  increases with increasing the amount of steel shavings in the charge and decreases with increasing the amount of coke. Maximum  $\alpha_{\text{Si(alloy)}}$  (85,06 %) is in the presence of 40 % of steel shavings and 46 % of coke. On the contrary, an increase in the amount of steel shavings reduces  $\alpha_{\text{Ca(CaC}_2\text{)}}$ , and an increase in the amount of coke in the charge increases  $\alpha_{\text{Ca(CaC}_2\text{)}}$ . Maximum  $\alpha_{\text{Ca(CaC}_2\text{)}}$  (68,4 %) is achieved at 8 % of steel shavings and 54 % of coke. To determine the optimal amounts of coke and steel shavings,  $\alpha_{\text{Si(alloy)}}$  and  $\alpha_{\text{Ca(CaC}_2\text{)}}$  should meet certain conditions. In our case it is:  $\alpha_{\text{Si(alloy)}} \geq 65 \%$  and  $\alpha_{\text{Ca(CaC}_2\text{)}} \geq 60 \%$ . Figure 2 shows combined information about  $\alpha_{\text{Si(alloy)}}$  and  $\alpha_{\text{Ca(CaC}_2\text{)}}$ .

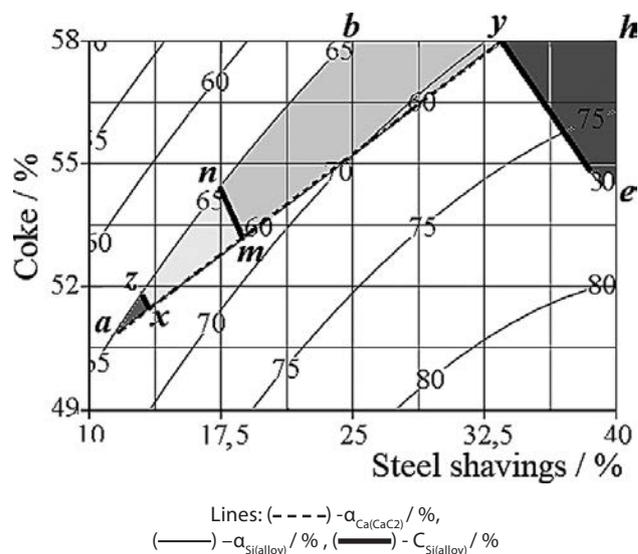


Figure 2 Combined information on the effect of coke and steel shavings on  $\alpha_{\text{Si(alloy)}}$ ,  $\alpha_{\text{Ca(CaC}_2\text{)}}$  and  $C_{\text{Si(alloy)}}$

Table 2 Technological parameters at the boundary of the axznmymhe area of Figure 2

Point in Figure 2	Values of independent variables		Technological parameters			
	Coke / %	Steel shavings / %	$\alpha_{\text{Si(alloy)}} / \%$	$\alpha_{\text{Ca(CaC}_2\text{)}} / \%$	$C_{\text{Si(alloy)}} / \%$	L / l/kg
a	50,8	11,8	65,0	60,0	48,3	148
z	51,5	12,5	65,0	60,0	47,0	157
x	51,2	12,9	65,9	58,0	47,0	149
n	54,2	17,1	65,0	64,1	41,0	165
m	53,1	18,4	67,8	60,0	41,0	158
y	58,0	33,2	70,0	60,0	30,0	148
h	58,0	40,0	71,4	53,4	27,7	139
e	53,4	40,0	77,8	44,8	30,0	129
b	58,0	25,0	65,0	67,3	35,8	167

The values of the technological parameters in the boundary marked areas are shown in Table 2.

FeSi45 ferrosilicon [19] is formed at 51,2-54,2 % of coke and 12,5-18,4 % of steel shavings (znmx area). Low-silicon FeSi25 ferrosilicon [19] can be obtained in the *yhe* region at 53,4-58 % of coke and 38,7-40 % of steel shavings. However,  $\alpha_{\text{Ca(CaC}_2\text{)}}$  in this case was 44,8-60 %. In the case of formation of FeSi45 ferrosilicon, calcium carbide is formed with a capacity of 149-165 l/kg, and in the case of formation of FeSi50 ferrosilicon, a capacity of the resulting calcium carbide is 148-152 l/kg. At the formation of FeSi25 ferrosilicon, the resulting calcium carbide is characterized by an even smaller capacity (128-167 l/kg). This calcium carbide can be used when growing vegetables on podzolic soils [20, 21].

## CONCLUSION

Based on the results obtained at the electric smelting of the Chilisyphosphorite, the following conclusions can be drawn:

At the producing siliceous ferroalloys, quartzite can be replaced with non-standard silica-containing natural, technogenic and artificial raw materials, including phosphorites containing up to 55 % of SiO<sub>2</sub>.

From a thermodynamic point of view, gaseous phosphorus, calcium carbide, and iron silicides can be simultaneously obtained from tricalcium phosphate in the presence of carbon, iron, and silicon dioxide at temperatures of more than 1 692,4 °C (in a case of FeSi) and more than 1 702,8 °C (in a case of FeSi<sub>2</sub>).

At the phosphorite's electric smelting, the effect of coke and steel shavings on the extraction degrees of silicon into the alloy and calcium into calcium carbide is opposite. The highest extraction degree of silicon into the alloy (85,06 %) was achieved at 40 % of steel shavings and 41 % of coke, and calcium into calcium carbide (68,4 %) – in a case of using the charge containing 10 % of steel shavings and 58% of coke.

FeSi45 ferrosilicon can be smelted from the phosphorite in the presence of 51,2-54,2 % of coke and 12,5-18,4 % of steel shavings; in this case  $\alpha_{\text{Si(ally)}}_{\text{Si}}$  is 65,0-67,8 %,  $\alpha_{\text{Ca(CaC}_2\text{)}}$  is 60,0-64,1 %, the resulting calcium carbide capacity is 148-165 l/kg.

Low-silicon FeSi25 ferrosilicon ( $C_{\text{Si}} = 27,7\text{-}30,0\%$ ) is formed at 53-58 % of coke and 39,7-40 % of steel shavings;  $\alpha_{\text{Ca(CaC}_2\text{)}}$  is 44,8-60 %; the calcium carbide capacity is 129-167 l/kg.

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**Note:** The responsible for English language is M.M. Yeskendirowa, M.Auezov South Kazakhstan University, Shymkent, Kazakhstan