International Journal of Mechanical Engineering and Technology (IJMET)
Volume 10, Issue 2, February 2019, pp; 1187-1197 Article ID: IJMET_10_02_123
Available online at http://www.iaeme.com/ijmet/issues.asp?JType=IJMET&VType=10&IType=2
ISSN Print: 0976-6340 and ISSN Online: 0976-6359

JOINT PRODUCTION OF CALCIUM CARBIDE AND A FERROALLOY OF THE DAUBABA DEPOSIT BASALT

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ABSTRACT

The present article contains the results of studying the electrothermal processing of the Daubaba deposit basalt (50.5% of SiO_2, 19.9% of Al_2O_3, 9.3% of CaO, 9.6% of Fe_2O_3,7.2% of MgO, 1.1% of TiO_2, 2.9% of $\sum (K_2O + Na_2O)$, 0.5% of MnO)) for production of calcium carbide and a ferroalloy. The basalt processing consisted in its electrosmelting in a monoelectrode arc furnace in graphite crucibles with diameter of 6 cm. The research was implemented using a second order rototable Box-Hunter plan. The subjects of interest were the effect of coke, steel cuttings and lime contents on the extraction degree of Si and Al in a ferroalloy and Ca in a technical calcium carbide; Si and Al concentration in the alloy obtained and a calcium carbide capacity. The result of simultaneous electrosmelting of the basalt, coke and steel cuttings was a ferroalloy containing 60.6% of (Si+Al) and calcium carbide with a capacity from 120 to 150dm^3/kg. When the basalt electrosmelting in the presence of 20-25% of lime, 11% of steel cuttings and 10% surplus of coke, calcium carbide of the $2^{nd}$and 3^{rd} grades with a *capacity of 233-240 dm^3/kg and complex ferroalloys of FS45A10 and FS45A15 grades containing 51.6-55.7% of ∑ (Si+Al) were obtained.*

Keywords: basalt, lime, electrosmelting, calcium carbide, ferroalloy, ferrosilicoaluminium.

Cite this Article; Viktor Mikhaylovich Shevko Gulnara Yergeshovna Karatayeva, Daniel Daniarovich Amanov Alexandra Dmitrievna Badikova And Gulvira Azatullaevna Bitanova, Joint Production of Calcium Carbide and A Ferroalloy of The Daubaba Deposit Basalt *International Journal of Mechanical Engineering and Technology* (IJMET) 10(2), pp;1187-1197
http://www.iaeme.com/ijmet/issues.asp?JType=IJMET&VType=10&IType=2

1. INTRODUCTION

Basalt is a rock, which makes up 25-38% of the Earth magmatic rocks [1]. Now basalt is mainly used for the manufacture of fibre [2-5]. Its insignificant part is applied for the manufacture of crushed stone, cast stone materials, acid-resistant powder, paving plates, stone blocks, facing plates and as a filler for concrete [6-11]. Basalt is a material rather stable against weather influence; therefore, it is often used for the exterior decoration finish of buildings and manufacturing of sculptures situated out-of-doors. Recently the market of the reinforcement produced from continuous basalt fibre is developing. However, at present, the basalt use efficiency is low. Therefore, the necessity of development of new competitive technologies on basalt processing and manufacture of basalt-based asked-for products is obvious. There are several basalt deposits in Kazakhstan. The Daubaba deposit situated in the south of the country is the largest one among them. Tephrite-basalt reserves of this deposit make 19.284 million tonnes, and leucite reserves – 5,154 million tonnes (∑ = 24.438 mil t) [12]. The prospects of C_2-class leucite gain are rather considerable. The chemical composition of the tephrite-basalts and leucites is represented in Table 1. The simultaneous SiO_2, Al_2O_3, CaO and Fe_2O_3 presence in the basalts is a reason of their application for manufacturing the production containing Si, Al, Ca and Fe. The article contains the research results of obtaining calcium carbide and a complex, Fe, Si and Al containing alloy of the Daubaba basalt.

Table 1 Composition of the Daubaba deposit tephrite-basalts and leucites

Rock	SiO_2	CaO	Al_2O_3	Fe_2O_3	TiO_2	MgO	Na_2O	K_2O	SO_3	∑ (K_2O+Na_2O)
Tephrite-basalt	43.15-67.2	5.5-11.87	14.03-18.1	7.65-9.97	0.6-1.3	4.36-8.05	-	-	0.03 -0.15	2.61 – 8.6
Leucite	40-47.26	5.58-14.42	13.65-15.12	3.42-13.6	-	2.98-9.92	1.7-5	2-5.9	0.09 -0.14	3.7 – 10.8

2. MATERIALS AND METHODS

The electrosmelting of a charge was implemented in a monoelectrode arc furnace lined with chromium-magnesite bricks. A hearth-level electrode has been made of a graphite block. A graphite crucible (d=6 cm, h=12 cm) was placed on a hearth. The space between the crucible and the lining was filled with graphite chips. The furnace top was covered by a demountable cover with apertures for the graphite electrode (d = 3 cm) and gas discharge. The medium is air. Before the smelting the crucible was heated by means of an electric arc within 20-25 minutes. After the heating the first charge portion (200 g) was loaded in the crucible and melted within 5-6 minutes; then the charge rest (200 g) was loaded and melted within 25-30 minutes.

During the electrosmelting the current intensity was 250-300A, voltage – 45-50V. A transformer TDZhF-1002 was used for supply of electricity to the furnace. The necessary power was supported by a thyristor regulator. The current intensity was controlled by means of an amperemeter Tangen 42L6 (accuracy class is 1.5), and the voltage – by a voltmeter Chint 42L6 (an accuracy class is 1.5). After the electrosmelting termination the furnace was cooled within 6 hours. The graphite crucible was pulled out of the furnace and broken. The calcium carbide and ferroalloy obtained were weighed and analyzed for determination of Fe, Si, Ca and Al content. The analysis of the raw materials and the ferroalloy was carried out using a scanning electronic microscope (SEM) JSM-6490LM (Japan), and also by means of an atomic adsorption method on a device ASS-IN (Germany) (the analysis error for the SEM makes <1%, and for the device AAS-IN – <0,3%). The elements' contents in the analyzed substances were calculated as the arithmetic mean of three analyses. The CaC2 content in the calcium carbide produced (C_{CaC_2}, %) was determined under the formula [13]:

$$C_{CaC_2} = (L/372) \div 100,\% \tag{1}$$

where La calcium carbide capacity (dm^3/kg): volume of the acetylene formed at calcium carbide decomposition with water according to the reaction $CaC_2+H_2O=C_2H_2+Ca\ (OH)_2$; 372 – volume of the acetylene formed at decomposition of 1 kg of 100% calcium carbide at 20°C and 760 mm Hg.

A calcium carbide capacity is a qualitative experimentally-found characteristic [14]. It can be calculated under the formula:

$$L = \frac{(p - p_1) \times 273 \times V}{(273 + t) \times 760 \times G}; \tag{2}$$

where p and p1 atmospheric pressure and water steam tension during the experiment, mm Hg;

V-volume of the acetylene liberated, ml;

G- calcium carbide weight, g;

T-temperature, °C;

L-a calcium carbide capacity, dm^3/kg.

The measurement error does not exceed 1-1.5%.

Besides the SEM analysis the total Si and Al content (C_{Si+Al}, %) in the alloy was determined on the basis of its density (D, g/cm^3). The density was measured by means of a pyknometer with application of kerosene. C_{Si} was calculated in accordance with the preliminary obtained formulas:

C_{Si+Al} = 690.679-545.783×D+166.151×D2-17.467×D3 (if D=3.52-6.09 g/cm^3); (3)

C_{Si+Al} = 130.878-21.232×D+0.859×D2 (if D=6.09-7.859 g/cm^3). (4)

The C_{Si+Al} determination error in this case did not exceed 2-2.5%.

The experimental extraction degree of calcium and aluminium from the charge into the technical calcium carbide can be calculated under the formula:

$$\alpha_{Ca(cc)} = \frac{G_{cc} \times C_{CaC_2} \times \frac{ACa}{MCaC_2}}{G_b \times C_{Ca(b)} + G_c \times C_{Ca(c)}} \times 100; \tag{5}$$

where G_b, G_c and G_{cc} – weights of the basalt, coke and technical calcium carbide, kg;

$C_{Ca\ (b)}$ and $C_{Ca\ (c)}$ – calcium content in the basalt and coke, %;

C_{CaC_2} – CaC_2 content in the technical calcium carbide, %;

ACa and $MCaC_2$ – calcium atomic weight and molecular calcium carbide weight.

The experimental silicon and aluminium extraction degree from the charge into the ferroalloy was calculated the following way:

$$\alpha_{Me(\text{alloy})} = \frac{G_{alloy} \times G_{Me}}{G_b \times C_{Me(b)} + G_c \times C_{Me(c)}} \times 100; \quad (6)$$

where G_{alloy} – the ferroalloy weight, kg;

$C_{Me\ (b)}$ and $G_{Me\ (c)}$ – silicon content in the basalt and coke, %;

C_{Me} – silicon (aluminium) concentration in the alloy, %.

The elemental composition of a basalt sample determined by means of the scanning electronic microscope is represented in fig. 1, and its derivatogram in fig. 2.

The microscopic analysis of the sample has shown that the Daubaba basalt contains: Si – 19.62%, Ca – 6.68%, Fe – 5.57%, Mg – 3.63%, Al – 8.61%, Mn – 0.24%, O – 53.03%, Na – 1.14%, P-0.28 %, K – 0.74%, Ti – 0.46%. Judging by fig. 2 at the homogeneous heating of the Daubaba basalt sample to 1000°C the mass loss of the substance makes 10.9%. The mass loss is connected with thermal decomposition of the rock and liberation of H_2O (5%), CO_2 (3.65%) and OH (2.25%). The basalt includes the following minerals: nontronite (50%), quartz (≈10%), calcite (8.3%), thermally inert substances (Fe_2O_3, MgO, CaO, fel spar, potassium-containing fel spar, etc.) (≈30%).

The X-ray phase analysis of a Daubaba basalt sample is represented in fig. 3. As follows from the analysis the basalt sample contains 51.8% of nontronite ($(Fe,Al)Si_2O_5(OH)\cdot H_2O$), 16.6% of calcite ($Ca(CO_3)$), 13.1% of magnesioferrite ($MgFe_2O_4$), 6.9% of quartz (SiO_2), 6.5% of albite (fel spar) ($Na(AlSi_3O_8)$), 5.1% of potassium-containing fel spar ($KAlSi_3O_8$).

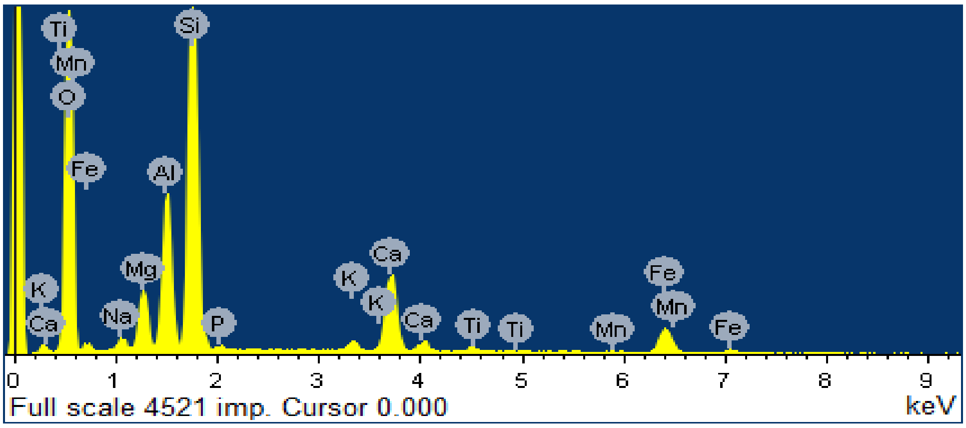


Figure 1 Scanning electronic microscopy of the basalt sample (the qualitative composition)

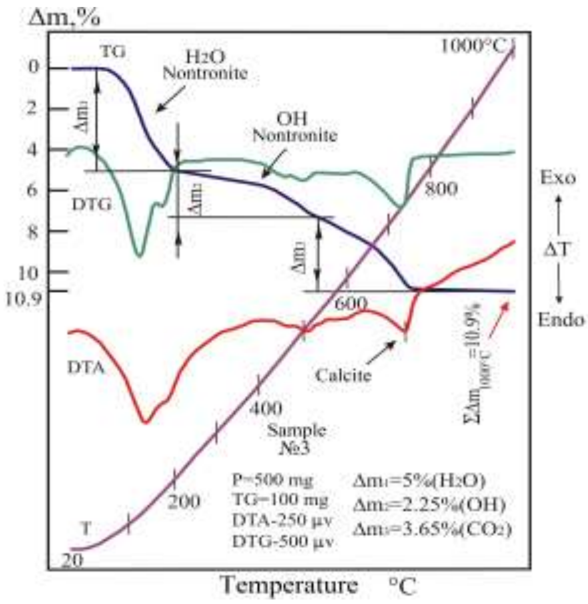


Figure 2 A derivatogramof the Daubaba deposit basalt sample

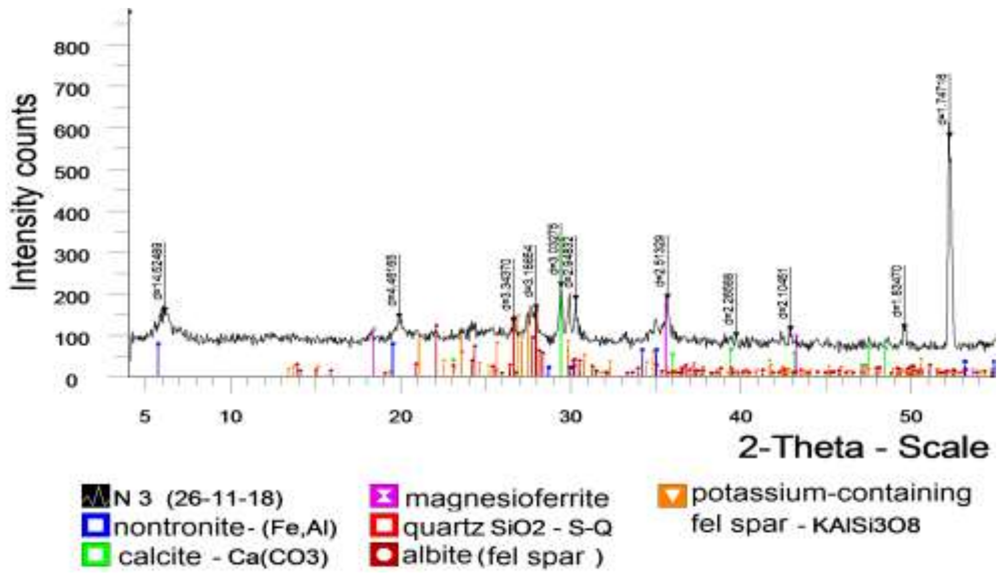


Figure 3 The X-ray phase analysis of the Daubaba deposit basalt sample

The ferroalloy and technical calcium carbide were obtained of the basalt containing after the calcination 50.5% of SiO_2, 18.9% of Al_2O_3, 9.3% of CaO, 9.6% of Fe_2O_3, 7.2% of MgO, 1.1% of TiO_2, 0.5% of MnO, 1.2% of K_2O, 1.7% of Na_2O. The coke contained 86% of C, 4.9% of SiO_2, 2.2% of Fe_2O_3, 1.8% of Al_2O_3, 1.5% of CaO, 0.8% of S, 0.4% of MgO, 1.3% of others, and the steel cuttings – 98.7% of Fe.

The research was implemented using a second order rototable Box-Hunter plan [15]. Subjects of the scientific research were the effect of coke (C) and steel cuttings (St) contents (% of the basalt mass) on the extraction degree of Si and Al in the ferroalloy and Ca in calcium carbide; Si and Al concentration in the alloy (C_{Si}, C_{Al}, C_{Si+Al}) and the technical calcium carbide capacity (L). The experiments' planning matrix and results are represented in table 2.

Table 2 The research planning matrix and results

#	Variables				Results					
	Code kind		Natural kind							
	X_1	X_2	Coke, %	St. cut., %	α_{Si}, %	α_{Al}, %	S_{isal}, %	C_{Si}, %	C_{Al}, %	L, dm^3/kg
1	-1	-1	41.5	12.2	78	69.2	55.8	45.6	10.2	113
2	+1	-1	48.5	12.2	73.1	65	58.6	50.3	8.3	140
3	-1	+1	41.5	17.8	80.8	61.3	47.9	35.5	12.4	98
4	+1	+1	48.5	17.8	75.1	77.6	54.1	44.1	10	129
5	+1.41	0	50	15	73.3	74	57.3	50.6	6.7	133
6	-1.41	0	40	15	80.6	64.5	52.4	41.8	10.6	100
7	0	1.41	45	19	77.6	74.4	50.1	39	11.1	107
8	0	-1.41	45	11	74.3	62	61.3	44.8	15.1	130
9	0	0	45	15	75	69.2	56	44	12	113
10	0	0	45	15	75.4	65.9	53.1	44.3	9.8	115
11	0	0	45	15	76.1	65.5	53.6	44.6	9	113
12	0	0	45	15	75.6	68.3	56.1	43.8	12.3	114
13	0	0	45	15	75.9	68.2	55.9	42.5	13.7	111

3. RESULTS AND DISCUSSION

The On the basis of the obtained results the following adequate regression equations were established:

$$\alpha_{Si}=428.881-11.326C+0.137St+8.7\cdot10^{-2}\cdot C^2+0.137\cdot St^2-0.326C\cdot St; \quad (7)$$

$$\alpha_{Al}=505.122-12.828\cdot C-23.604St+0.035\cdot St^2+0.522C\cdot St+0.065\cdot C^2; \quad (8)$$

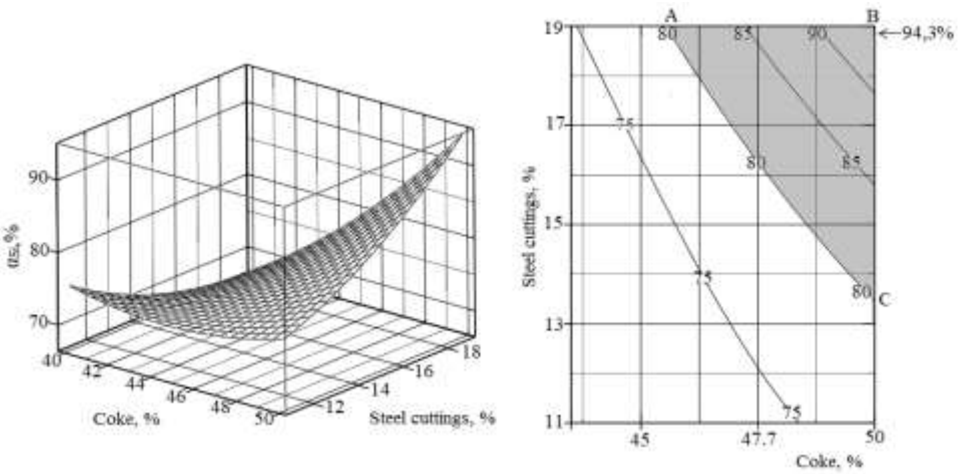
$$C_{Si}=244.756-1.690C-0.129\cdot C^2-8.920\cdot St+0.099St\cdot C+0.092\cdot St^2; \quad (9)$$

$$C_{Al}=157.537-4.403C+0.164\cdot C^2-0.105St^2-0.015C\cdot St-9.350\cdot St; \quad (10)$$

$$C_{Si+Al}=53.266-5.492St+0.010\cdot St^2+1.756\cdot C-0.027\cdot C^2+0.086C\cdot St; \quad (11)$$

$$L=523.112-19.736St+0.417St^2-14.506\cdot C+0.102C\cdot St+0.185C^2. \quad (12)$$

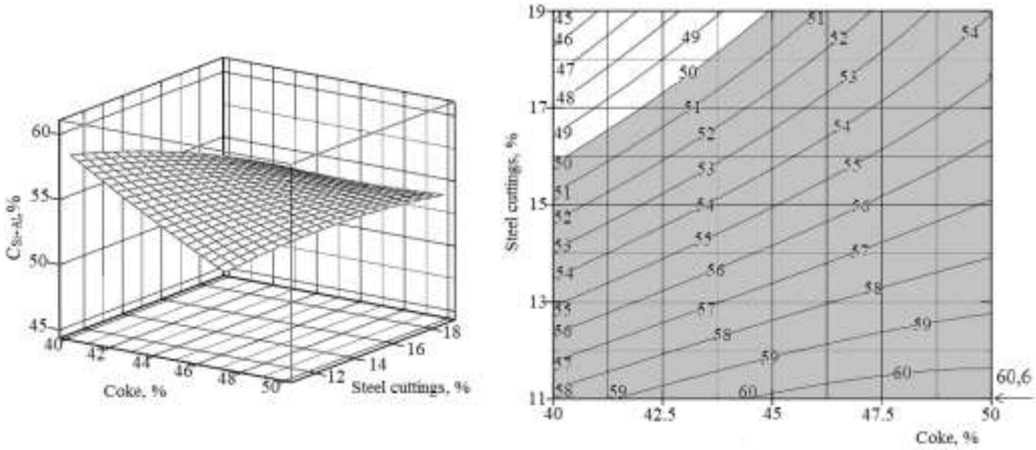
Using equations 7-12 and the technique [16] we constructed 3D images of response surfaces and their horizontal sections. The three-dimensional surfaces and their horizontal sections for α_{Si} and C_{Si+Al} are shown in fig. 4 and 5, the horizontal sections for αSi and L in fig. 6, respectively. As follows from the figures, the increase of the coke quantity raises α_{Si}, α_{Al}, C_{Si+Al}, C_{Si}, α_{Al} and L. The increase of the steel cuttings quantity increases α_{Si}, α_{Al} and decreases C_{Si+Al}, C_{Si}, the calcium carbide capacity. The influence of steel cuttings on C_{Al} has the complex and ambiguous nature.



Numerals on lines – α_{Si},%

I – three-dimensional image, II – horizontal sections

Figure 4. Effect of the coke and steel cuttings quantity on α_{Si}



Numerals on lines – C_{Si+Al}, %

I – three-dimensional image, II – horizontal sections

Figure 5. Effect of the coke and steel cuttings quantity on C_{Si+Al}, %

Judging by fig. 4 α_{Si} from 80 to 94.3% can be reached in the ABC area. C_{Si+Al} from 50 to 60.6% is observed in the dark area of figure 5. The Al extraction degree in the alloy from 75 to 88.6% is possible in the XYZ area (fig. 6 (I)). A capacity of the calcium carbide produced does not exceed 150 dm^3/kg (fig. 6 (II)). This calcium carbide can be used for increasing of productivity of vegetables [17]. However, a demand for it is low. The calcium carbide capacity (at the given stage) is a limiting factor of the technology. Fig. 7 was constructed on the basis of a condition of obtaining the calcium carbide with a capacity more than 120dm^3/kg, $\alpha_{Si} \geq 80\%$ and $C_{Si+Al} \geq 52.5\%$.

III

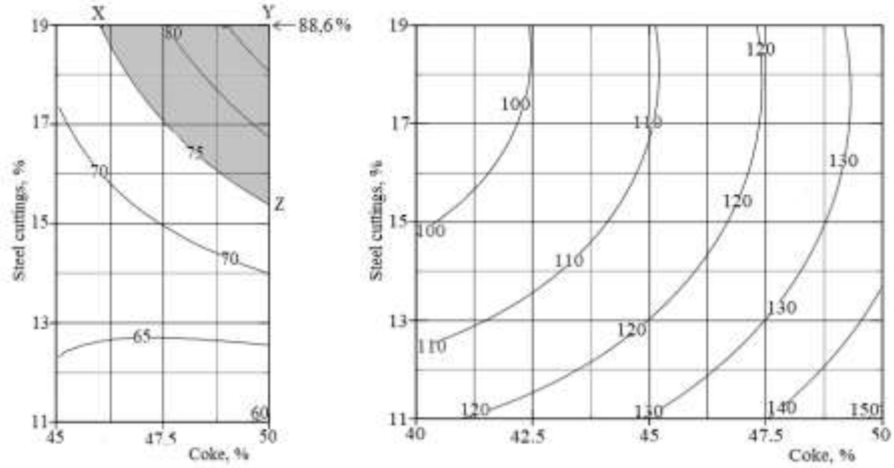
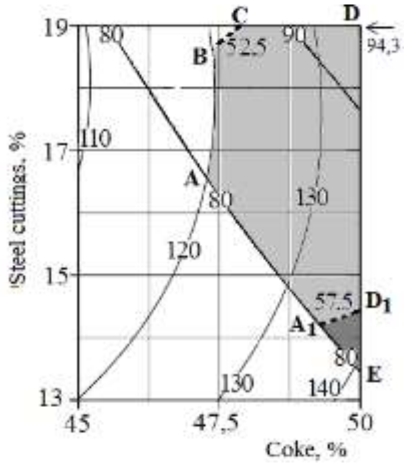


Figure 6 Effect of the coke and steel cuttings quantity on α_{Al}(I), L(II)



(-) – L, dm^3/кг; () – α_{Si},%; (- -) – C_{Si+Al},%

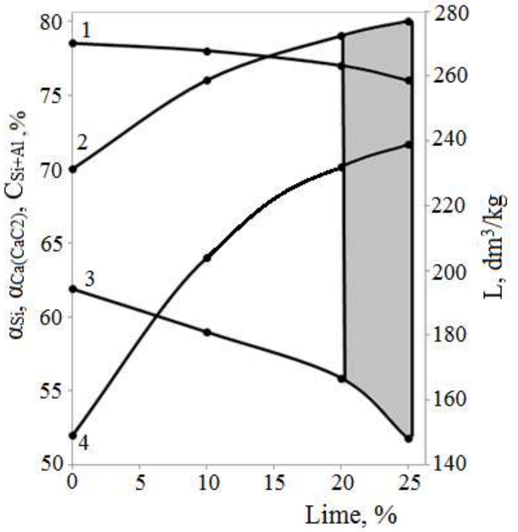
Figure 7 Superimposed information about the coke and steel cuttings influence on the technological parameters of electrosmelting the Daubaba basalt

Table 3 contains the information about the coke and steel cuttings quantity and technological parameters in boundary points of fig. 7.

Table 3. Values of technological parameters and coke and steel cuttings quantities in boundary points of fig.7

Point on figure7	α_{Si}, %	α_{Al}, %	C_{Si}, %	C_{Si+Al}, %	L, dm^3/kg	Coke, %	Steel cuttings, %
A	80.0	73.3	73.3	54.5	120.0	47.28	16.60
B	84.7	78.7	78.67	52.5	120.0	47.38	18.70
C	87.0	81.1	81.1	52.5	122.8	47.87	19.00
D	94.3	88.6	88.6	53.96	134.8	50.00	19.00
E	80.0	68.1	68.1	58.4	140.8	50.00	13.46
A_1	80.0	70.0	70.0	57.5	134.5	49.27	14.22
D_1	82.0	71.6	71.6	57.5	137.8	50.00	14.45

As follows from the data of table 2, the ABCDE area is characterized by the following indicators: the calcium carbide capacity is 120-140.8 dm^3/kg, ∑(Si+Al) content in the ferroalloy is from 52.5 to 58.4%. So, the elements' extraction degrees in the alloy make: Si – 80-94.3%, Al – 68.1-88.6%. In the $ABCDD_1A_1$ area at 47.28-50% of coke and 14.22-19% of steel cuttings α_{Si} is 80-94.3%, α_{Al} – 68.1-88.6%, L – 120-134.5 dm^3/kg and C_{Si+Al} – 52.5-57.5%. The ferroalloy containing ∑(Si+Al) from 57.5 to 58.4% is formed in the A_1D_1E area at 49.27-50% of coke, 13.46-14.45% of steel cuttings. In this area α_{Si} makes 80-82%, α_{Al} – 68.1-71.6%, L – 134.5-140.8 dm^3/kg. The calcium carbide formed in view of the low CaO content in the basalt is characterised by a low capacity. For increase of the calcium carbide capacity, lime was added in the charge (94.7% of CaO, 0.5% of MgO, 0.3% of SiO_2, 0.2% of Al_2O_3, <0.1% of MnO, calcination losses – 4.3%). The lime effect on the process technical characteristics is shown in fig. 8. At the implementation of this series of experiments the quantity of steel cuttings was constant – 11% of the basalt weight. The coke mass was calculated proceeding from 110% of the theoretical quantity necessary for full reduction of Si, Al, Fe and formation of CaC_2.



1 – α_{Si}, 2 – $\alpha_{Ca\,(CaC2)}$, 3 – C_{Si+Al}, 4 – L

Figure 8 Effect of lime quantity on technological parameters of the Daubaba basalt electrosmelting process

Judging by fig.8, the increase of the lime quantity promotes the growth of the calcium carbide capacity to 240 dm^3/kg and the extraction degree of Ca in CaC_2 to 80.3%. At the same time the silicon extraction degree in the alloy and total silicon and aluminium concentration in the alloy decrease to 76.1% and 51.6%, respectively. In the shaded area of fig.8 the formed calcium carbide has a capacity of 233-240 dm^3/kg that corresponds to its 2nd and 3rd grades in accordance with [18], and the ferroalloy contains 51.6-55.7% of C_{Si+Al} and complies with a complex ferroalloy – ferrosilicoaluminium of FS45A10 and FS45A15 grades [19].

The influence of lime (Lm) (from 0 to 25% of the basalt weight) on the technological parameters can be described by the equations:

$$\alpha_{Ca(CaC2)}= 70.124+0.6981\cdot Lm-0.0122\cdot Lm^2; \quad (13)$$

$$\alpha_{Si}=78.382-0.0107\cdot Lm-0.0031\cdot Lm^2; \quad (14)$$

$$L= 140.49+8.0274\cdot Lm-0.164\cdot Lm^2; \quad (15)$$

$$C_{Si+Al}=62.985-0.4153\cdot Lm. \quad (16)$$

4. CONCLUSION

On the basis of the results obtained the following conclusions can be drawn:

at the electrosmelting the basalt in the presence of 46.6-50% of coke and 13.5-19.8% of steel cuttings there is the simultaneous formation of calcium carbide with a capacity of 120-

150dm^3/kg (it can be used as a growth regulator for vegetables) and ferroalloys of FS45A10 and FS45A15 grades containing 52.5-58.6% of ∑(Si+Al); Si and Al extraction degrees in the alloy are 80-94.3 and 68.1-88.6%, respectively;

the basalt electrosmelting at the presence of lime allows to increase the extraction degree of calcium in CaC_2 and to raise the calcium carbide capacity; when the basalt is melted at presence of 11% of steel cuttings, 20-25% of lime and 10% excess of coke (% of the basalt weight) there is formation of calcium carbide of the 2nd and 3rdgrades with a capacity of 233-240dm^3/kg and ferrosilicoaluminium with the total silicon and aluminium content of 51.6-55.7%; in this case the silicon extraction degree in the alloy makes 76.1-77.2%, calcium in the calcium carbide – 79.1-80.3%.

5. ACKNOWLEDGEMENT

The research has been implemented at support of the Ministry of Education and Science of the Republic of Kazakhstan as grant financing on the theme “Combined production technology of ferroalloys and calcium carbide from nonconventional natural raw materials and the technogenic wastes containing high-clarke elements”.

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