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SHEVKO V.M., BADIKOVA A.D., TULEEV M.A., KARATAEVA G.E.

M.Auezov South Kazakhstan State University, Shymkent, Kazakhstan
E-mail: shevkovm@mail.ru

KINETICS OF EXTRACTION OF THE SILICON, ALUMINUM AND CALCIUM OF THE BASALT FROM THE DAUBABA DEPOSIT

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Abstract. The article presents the results of the experimental studies of the kinetics of electric smelting of the basalt from the Daubaba deposit, the main components of which are 50.5% SiO_2, 19.9% Al_2O_3, 9.3% CaO, 9.6% Fe_2O_3 with the extraction of the silicon and aluminum into the ferroalloy, calcium into the calcium carbide. The effect of electric smelting time (from 10 to 60 minutes) and the amount of lime (from 0 to 30% from weight of basalt) on the degree of extraction of Si and Al into the alloy and Ca into CaC_2 was determined. The studies were carried out by the method of planning the experiments with the usage of roto-standard plans of second order (Box-Hunter plan) with exploring graphic optimization of technological parameters. The electric smelting was carried out in a graphite crucible. The mass of the furnace-charge in each experiment was 400 g. It was found that: extraction of Si, Al into the alloy, and Ca into the calcium carbide becomes noticeable in the first 10 minutes of the process; in the absence of lime, the maximum degree of extraction of the silicon, aluminum in the alloy and the calcium, respectively, contain 80.8%, 72.2% and 69% in 45 minutes; the presence of lime in the furnace-charge allows you to increase the degree of extraction of the calcium in the calcium carbide to 79.8%, however, at this time, the extraction of the silicon and aluminum decreases. To extract 77.1-86.8% of the silicon, 75-82% of the aluminum in the alloy and 75-79% of the calcium in the calcium carbide, the duration of the electric smelting should be 46-50 minutes and the amount of lime to 6.1% from weight of basalt.

Keywords:basalt, coke, lime, steel chip, electric smelting, time, ferroalloy, calcium carbide.

ШЕВКО В.М., БАДИКОВА А.Д., ТУЛЕЕВ М.А., КАРАТАЕВА Г.Е.

М. Ауэзоватындағы Оңтүстік-Қазақстан мемлекеттік университеті, Шымкент, Қазақстан
E-mail: shevkovm@e.mail.ru

ДАУБАБА КЕНОРНЫНЫҢ БАЗАЛЬТЫНАН КРЕМНИЙ, АЛЮМИНИЙ ЖӘНЕ КАЛЬЦИЙ БӨЛІП АЛУ КИНЕТИКАСЫ

Түйіндеме. Мақалада кальций карбидіне кальцийді, ферроқорытпаға алюминийді, кремнийді бөліп алу арқылы негізгі компоненттері 50,5% SiO_2, 19,9% Al_2O_3, 9,3% CaO, 9,6% Fe_2O_3 болып табылатын Даубаб кен орнындағы базальтты электрлі балқыту кинетикасын эксперименттік зерттеу нәтижелері келтірілген. CaC_2-ге Са және қорытпаға Si және Al бөліп алу дәрежесіне(0-ден 30% дейін базальттың массасына байланысты) әктасты мөлшері мен электрлі балқыту уақытының (10-нан 60 минутқа дейін) әсері анықталды. Зерттеу технологиялық параметрлердің зерттелетін графикалық оптимизациясымен (Бокса-Хантер жоспары) екінші тәртіптегі рототабельді жоспарды қолдану арқылы эксперименттерді жоспарлау әдісімен жүргізілді.Электрлі балқытуграфитті тигельде жүргізілді. Әрбір тәжірибеде шихтаның массасы 400 г. құрайды. Анықталды: қорытпаға Si, Al және кальций карбидіне Са бөліп алу процестің бастапқы 10 минут ішінде байқала бастайды; әктас болмауы қорытпаға алюминийді, кремнийді және кальцийдібөліп алудың максимальды дәрежесі 45 минут ішінде сәйкесінше 80,8%, 72,2% және 69% құрайды; шихтада әктастың болуы кальций карбидіне кальцийді бөліп алу дәрежесін 79,8% дейін арттыруға мүмкіндік береді, бірақ, бұл кезде кремний мен алюмнийді бөліп алу дәрежесі төмендейді. Қорытпаға 77,1-86,8% кремнийді, 75-82% алюминийді және кальций карбидіне 75-79% кальцийді бөліп алу үшін электрлі балқыту ұзақтылығы 46-50 минутты және базальттың массасына байланыстыәктастың мөлшері 6,1% құрайды.

Түйін сөздер: базальт, кокс, әктас, болат жоңқасы, электрлі балқыту, уақыт, ферроқорытпа, кальций карбиді.

ШЕВКО В.М., БАДИКОВА А.Д., ТУЛЕЕВ М.А., КАРАТАЕВА Г.Е.

Южно-Казахстанский государственный университетим. М. Ауэзова, Шымкент, Казахстан
E-mail: shevkovm@e.mail.ru

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КИНЕТИКА ИЗВЛЕЧЕНИЯ КРЕМНИЯ, АЛЮМИНИЯ И КАЛЬЦИЯ ИЗ БАЗАЛЬТА МЕСТОРОЖДЕНИЯ ДАУБАБА

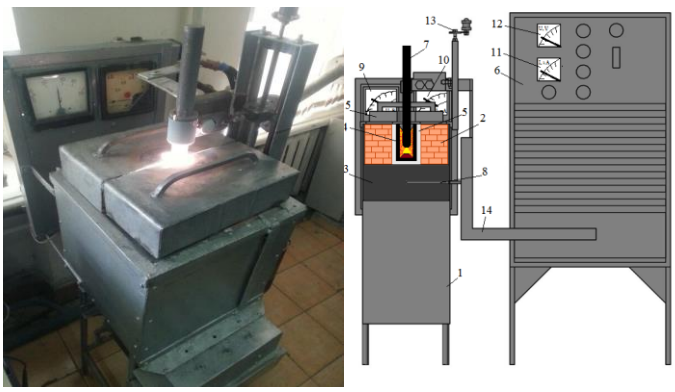
Аннотация. В статье приводятся результаты экспериментальных исследований кинетики электроплавки базальта месторождения Даубаба основными компонентами которого являются 50,5% SiO_2, 19,9% Al_2O_3, 9,3% CaO, 9,6% Fe_2O_3 с извлечением кремния и алюминия в ферросплав, кальция в карбид кальция. Определялось влияние времени электроплавки (от 10 до 60 минут) и количества извести (от 0 до 30% от массы базальта) на степень извлечения Si и Al в сплав и Ca в CaC_2. Исследования проводились методом планирования экспериментов с использованием рототабельных планов второго порядка (план Бокса-Хантера) с исследующей графической оптимизацией технологических параметров. Электроплавка проводилась в графитовом тигле. Масса шихты в каждом опыте составляла 400 г. Найдено, что: извлечение Si, Al в сплав и Ca в карбид кальция становится заметным в первые 10 мин процесса; в отсутствии извести максимальная степень извлечения кремния, алюминия в сплав и кальция соответственно составляют 80,8%, 72,2% и 69% за 45 минут; присутствие извести в шихте позволяет увеличить степень извлечения кальция в карбид кальция до 79,8%, однако извлечение кремния и алюминия при этом уменьшается. Для извлечения 77,1-86,8% кремния, 75-82% алюминия в сплав и 75-79% кальция в карбид кальция продолжительность электроплавки должна быть 46-50 минут и количество извести до 6,1% от массы базальта.

Ключевые слова: базальт, кокс, известь, стальная стружка, электроплавка, время, ферросплав, карбид кальция.

Introduction. A promising direction in the development of metallurgy is the combination of the processes of obtaining several products in a single furnace unit. Such combination makes it possible to reduce not only the heat consumption through the brick lining, but also to involve in the production sphere a new raw material with the large reserves. This category of raw materials includes the igneous rock - basalt (igneous rocks according to the data [1] occupy 25-38% of the earth's surface). In the view of the fact that the raw material potential of the basalt is not used fully, we have proposed a technology of simultaneous electro-thermal production of the calcium carbide and ferroalloy from the basalt in order to expand the possibilities of its processing [2-4]. The article presents the results of the experimental studies of the kinetics of the extraction of the silicon, aluminum into the ferroalloy and calcium into the calcium carbide from the basalt of the Daubaba deposit, the reserves of which contain 19.4 million tons [5].

Experimental part. The electric smelting of the furnace-charge (basalt, coke, steel chip, and lime) was carried out in a single-electrode lined arc furnace (Figure 1). The bottom electrode was made of a graphite block. A graphite crucible was installed on the bottom (d=6 cm, h=12 cm). The space between the crucible and the lining was filled with the graphite chips. The furnace in the upper part was closed with a removable cover with the holes for a graphite electrode (d=3 cm) and a gas outlet. Before the melting, the crucible was heated by an arc during 20–25 min. After that, the crucible was loaded with the first portion of the furnace-charge (200 g). It was melted for 5-6 minutes, and then the rest of the furnace-charge (200 g) was loaded and melted for the required time. Electricity in the furnace was fed from a transformer TAFT-1002. The required power was maintained by a terristor regulator. The control of the current power was monitored with an ampere meter as Tangen 42L6 (an accuracy class 1.5) and the voltages with the voltmeter as Chint 42L6 (an accuracy class 1.5). After electric smelting, the hot crucible was removed from the furnace and cooled for 5-6 hours. Then the graphite crucible was smashed. Carbide and ferroalloy were weighed and analyzed for Fe, Si, Ca and Al.

I II



1 - furnace casing, 2 - chrome-magnesite lining, 3 - carbon-graphite bottom, 4 - graphite crucible, 5 - carbon-graphite "cushion", 6 - transformer TAFT-1002,7 - graphite electrode, 8 - lower current lead, 9-12 controlling ampere meters andvoltmeters, 13 - the mechanism of the moving the electrode, 14 - the flexible part of the short network, 15 - the furnace cover
I - general view, II - sketch of the furnace with the knots
Figure 1 - Single-electrode lined arc furnace

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In all experiments, the amount of coke and steel chip was constant and contained 120% from the theoretically necessary for the reduction of the silicon, aluminum, iron to the metal, and the calcium to the calcium carbide and 15% from the mass of basalt, respectively.

Analysis of the raw materials and products of the electric smelting was carried out by the method of scanning electron microscopy (JSM-6490LM device (Japan)), by atomic adsorption method (AAS-1N device, (Germany)) by X-ray diffraction method (Dron-3 automated diffractometer device). The concentration of Si+Al in the alloy was also determined by the pycnometric method (through the density) using the equations we published earlier [6].

The degree of extraction of the silicon and aluminum in the alloy was determined by the ratio of the mass of the metal in the alloy to the mass of the metal in the furnace-charge. The degree of calcium extraction to the technical calcium carbide (α_{Ca}, %) was determined by the formula:

$$\alpha_{Ca} = \frac{G_{cc} \cdot C_{CaC_2} \cdot 0.625}{G_{bas} \cdot C_{Ca(bas)} + G_{lime} \cdot C_{Ca(lime)}} \cdot 100 \qquad (1)$$

where G_{bas}, G_{lime}иG_{cc} – respectively, the mass of basalt, the mass of lime and the mass of calcium carbide, g;

$C_{Ca(bas)}$, $C_{Ca(lime)}$ - respectively, the content of the calcium in the basalt, lime, share 1;

0.625 - is the ratio of the atomic mass of calcium to the molecular mass of the calcium carbide;

C_{CaC_2} - is the concentration of CaC_2 in technical calcium carbide, fraction 1, which is determined from the expression:

$$C_{CaC_2} = L / 372, \qquad (2)$$

in which L is the liter of calcium carbide, dm^3/kg (determined experimentally by the method [7]), 372 is the amount of acetylene (dm^3) released during the interaction of 1 kg of CaC_2 with water.

Figure 2 shows the result of scanning electron microscopy of the basalt surface, from which it follows that the basalt contains 50.5% SiO_2, 19.9% Al_2O_3, 9.3% CaO, 9.6% Fe_2O_3, 7.2% MgO, 1.1% TiO_2, 2.9% ∑K_2O and Na_2O, 0.5% MnO. Or 21.15% Si, 6.68% Ca, 4.28% Fe, 3.55% Mg, 9.55% Al, 0.18% Mn, 51.01% O, 1.09% Na, 1.23% P, 0.87% K, 0.40 Ti. By X-ray phase analysis (Figure 3), it is found that Daubaba basalt contains 51.8% nontronite [(Fe, Al) $Si_2O_5OH \cdot H_2O$], 16.6% calcite ($CaCO_3$), 13.1% magnesitoferrite ($MgFe_2O_4$), 6.9% quartz (SiO_2), altite [$Na(AlSi_3O_8)$], 5.1% calcium aluminosilicate ($KAlSiO_8$). Lime contained ≥ 94% SiO_2, coke 85-87% C, and steel chip - 98.7% Fe.

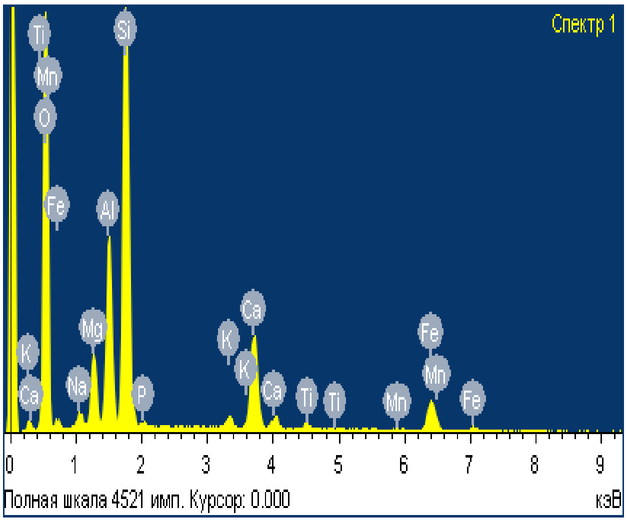

Figure 2 - Scanning electron microscopy of a sample of the basalt (qualitative composition)

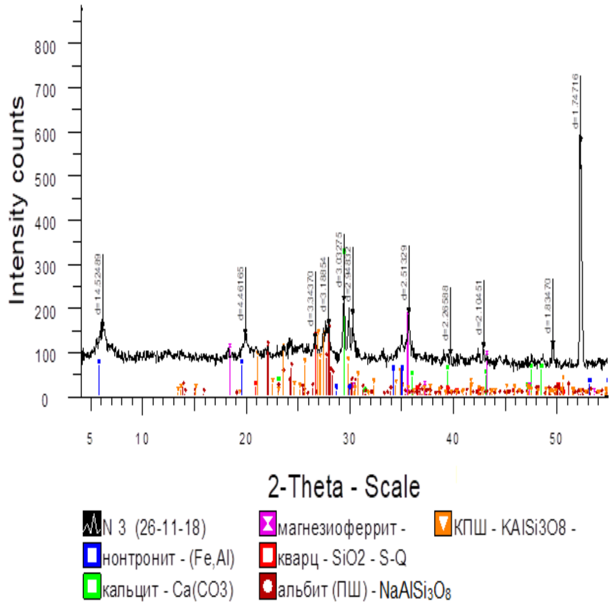

Figure 3 - X-ray phase analysis of the basalt samples from the Daubaba deposit

Results and Discussion. Figures 4 show the effect of time on the degree of transition of the silicon, aluminum to the ferroalloy and the calcium to the calcium carbide, from which it follows that electric smelting of the basalt without lime occurs effectively up to 45 minutes. Moreover, according to the degree of transition of the metals into the target products, the metals form a series: α_{Si} (80.8%) >α_{Al} (72.2%) >α_{Ca} (69.0%). The inflection at 45

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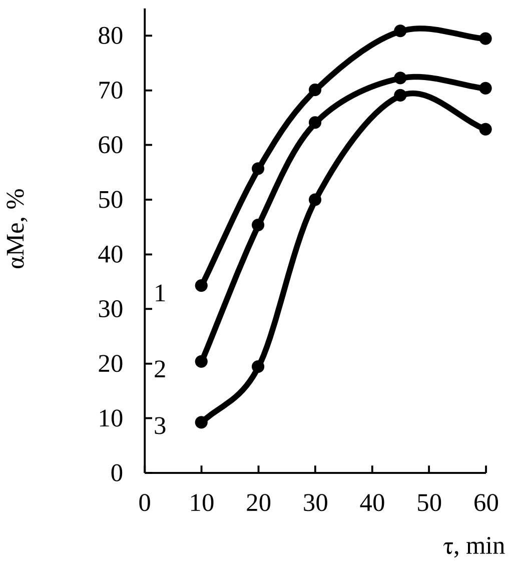
minutes for α_{Ca} is associated with the decomposition of CaC_2 [8]. Found that the time of electric smelting affects the degree of transition of metals in the alloy and carbide in accordance with the equations:

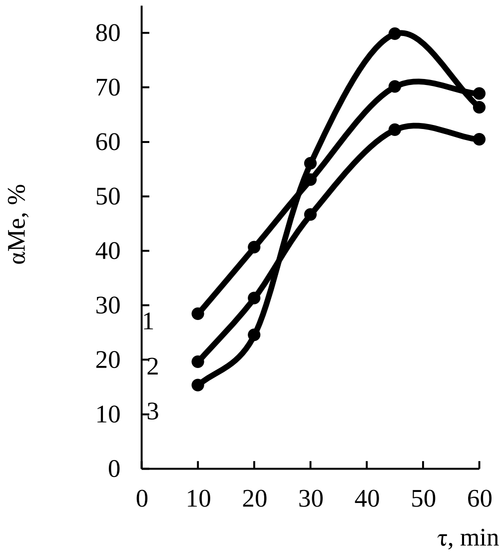
$\alpha_{Si} = 7.9315 + 2.9469 \cdot \tau - 0.0293 \cdot \tau^2;$ (3)
$\alpha_{Al} = -18.026 + 4.433 \cdot \tau - 0.067 \cdot \tau^2 + 3 \cdot 10^{-4} \cdot \tau^3;$ (4)
$\alpha_{Ca} = 71.294 - 12.09 \cdot \tau + 0.7191 \cdot \tau^2 - 1.4 \cdot 10^{-2} \cdot \tau^3.$ (5)

The content of the basalt of calcium oxide is less than the oxide of the silicon and aluminum. Calcium carbide formed during the electric smelting of the basalt was poorly formed into an independent phase and had a low displacement (no more than 80 dm^3/kg), therefore the following series of experiments was carried out (25% of basalt mass). Figure 5 shows the effect of the time of the electric smelting of the basalt with lime on the degree of transition of metals into the products, from which it can be seen that the maximum extraction of metals falls on 50 minutes. In the presence of lime, α_{Ca} increased to 79.8%, while aα_{si}иα_{Al} decreased. In 50 minutes, α_{Ca} (79.8%) >α_{Si} (70.1%) >α_{Al} (62.2%). The effect of time on the extraction of metals in the alloy and calcium carbide in the smelting of basalt in the presence of lime is described by the equations:

$\alpha_{Si} = 23.324 + 0.0849 \cdot \tau + 0.0505 \cdot \tau^2 - 7 \cdot 10^{-4} \cdot \tau^3;$ (6)
$\alpha_{Al} = 13.294 + 0.1752 \cdot \tau + 5.1 \cdot 10^{-2} \cdot \tau^2 - 7 \cdot 10^{-4} \cdot \tau^3;$ (7)
$\alpha_{Ca} = 82.337 - 12.849 \cdot \tau + 0.7491 \cdot \tau^2 - 1.43 \cdot 10^{-2} \cdot \tau^3.$ (8)



1 - Si, 2 - Al, 3 - Ca
Figure 4 – The influence of the time of electric smelting of Daubaba basalt (without lime) on the degree of extraction of Si, Al into the alloy and Ca into the calcium carbide



1 - Si, 2 - Al, 3 - Ca
Figure 5 - The effect of the time of electric smelting of Daubaba basalt (with 25% lime) on the degree of extraction of Si, Al into the alloy and Ca into the calcium carbide

Taking into account the complicated nature of the influence of time of electric smelting of basalt and lime on the behavior of metals (Figure 4, 5), we carried out the studies, using the method of experiment planning and using the roto-standard planning of second order with subsequent graphic optimization [9]. The experiments were carried out in accordance with the conditions, given in the table 1.

Table 1 - Planning matrix and results of experiments on electric smelting of Daubaba basalt

№	Variable				α_{Si}, %	α_{Al}, %	α_{Ca}, %
	Coded view		Natural view				
	X_1	X_2	Lime (li), %	t, min			
1	+1	+1	25.6	44.2	63.4	61.3	78.6
2	+1	-1	25.6	15.8	35.2	25.2	24.2
3	-1	+1	4.4	44.2	74.0	68.5	73.7
4	-1	-1	4.4	15.8	41.3	31.0	16.8
5	1.414	0	30.0	30.0	48.1	35.3	61.4
6	-1.414	0	0.0	50.0	70.6	64.0	49.2
7	0	1.414	15.0	10.0	72.2	68.1	81.0
8	0	-1.414	15.0	30.0	30.1	20.5	15.6

Based on the data in the Table 1, the following regression equations are obtained:

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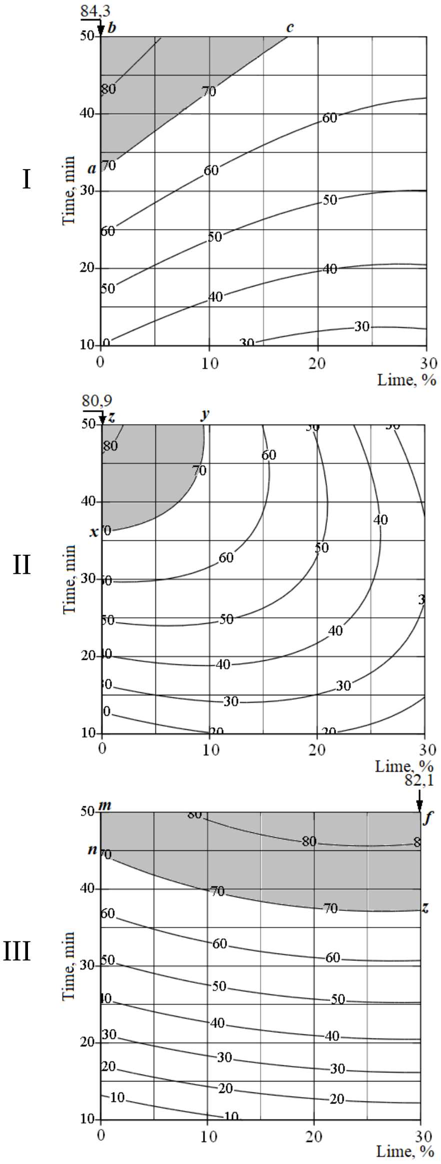
α_{Si} = 23.48 - 0.948·Li - 1.73·τ + 2· Li^2 - 9.3·10^{-3}·τ^2 - 7.47·10^{-3}· Li·τ; (9)

α_{Al} = -23.34 + 1.72· Li + 3.84·τ - 0.037· Li^2 - 3.43·10^{-2}·τ^2 - 5.26·10^{-2}· Li·τ; (10)

α_{Ca} = -29.98 + 0.89·Li + 3.36·τ - 1.4·10^{-2}· Li^2 - 2.51·10^{-2}·τ^2 - 4.15· Li·τ (11)

Using the equations (9)-(11), in accordance with [10] the dependences of the effect of lime and time on α_{Si}, α_{Al}, α_{Ca} were constructed (Figure 6).



The numbers on the lines - the degree of metal extraction, %

I - α_{Si} into the alloy, II - α_{Al} into the alloy,
III - α_{Ca} into the carbide calcium

Figure 6 - The effect of lime and time on the degree of transition of metals into the ferroalloy and calcium carbide

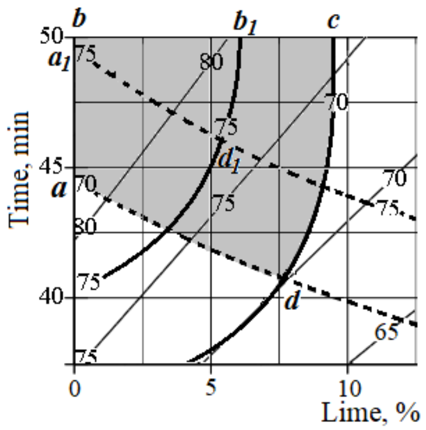
From the Figure6, it follows that α_{Si} from 70 to 84.3% is observed in the abc region, α_{Al} from 70 to 80.9% - in the xyz region and α_{Ca} - from 70 to 82.1% in the nmfz region.

In choosing the optimal conditions, we proceeded from the need to extract at least 70% of the metal into the products. Figure 6 shows the abcd area that meets these conditions. Table 2 shows the technological parameters around the perimeter of the abcd area, in which when the amount of lime varies from 0 to 9.4 within 40.7-50 minutes, the degree of extraction of silicon into the alloy contains 70-86.6%, aluminum - 70-82.0% and calcium in the calcium carbide - 70-80.6%.

Table 2- The values of technological parameters around the perimeter of the abcd area of the Figure 7.

Point in the figure 7	Technological parameters				
	Lime, %	Time, min	α_{Si}, %	α_{Al}, %	α_{Ca}, %
a	0.0	44.6	82.2	78.8	70.0
b	0.0	50.0	86.8	82.0	75.4
c	9.4	50.0	76.2	70.2	80.6
d	7.7	40.7	70.1	70.0	70.0
a_1	0.0	49.5	86.4	81.8	75.0
b_1	6.1	50.0	79.5	75.0	79.0
d_1	5.4	46.0	77.1	75.0	75.0

A higher degree of extraction of the silicon, calcium and aluminum is observed in the $a_1bb_1d_1$ region, in which α_{Si} = 77.1%, α_{Ca} = 75-79%, α_{Al} = 75-82% for 46-50 minutes and lime to 6.1% from the slag mass.



(- -) - α_{Ca}, (▬▬) - α_{Al}, (——) - α_{Si}

Figure 7 - The optimal transition region of silicon, aluminum in the alloy and calcium to the calcium carbide

Conclusions. Based on the results, obtained on the kinetics of the electric smelting of basalt from the Daubaba deposit, the following conclusions can be drawn:

- the extraction of Si, Al into the alloy and Ca into the calcium carbide becomes noticeable in the first 10 minutes of the process; in the absence of lime, the maximum degree of extraction of the silicon, aluminum in the alloy and the calcium, respectively, contain 80.8%, 72.2% and 69% in 45 minutes;

- the presence of 30% lime in the furnace-charge allows to increase the degree of calcium extraction into the calcium carbide up to 82.1%, however, at this time the extraction of the silicon and aluminum decreases;

- in the optimal technological area up to 6.1% of lime, for 46-50 minutes the extraction of the silicon and aluminum in the alloy is 77.1-86.8% and 75.0-82.08%, and α_{Ca} in the calcium carbide - 75-79%.

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Information about authors: M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan
Shevko Viktor Mikhailovich- doctor of technical sciences, professor of M. Auezov South Kazakhstan State University. https://orcid.org/0000-0002-9814-6248, e-mail: shevkovm@mail.ru
Badikova Alexandra Dmitrievna- master of engineering and technology, specialist junior researcher of M. Auezov South Kazakhstan State University.https://orcid.org/0000-0003-0027-4258, e-mail: sunstroke_91@mail.ru
Tuleev Mustafa Azatovich- master of technical sciences, a specialist of higher educational qualifications of M. Auezov South Kazakhstan State University.https://orcid.org/0000-0002-1439-8676, e-mail: mustafa19930508@mail.ru
Karataeva Gulnara Ergeshovna - candidate of technical sciences, associate professor of M. Auezov South Kazakhstan State University.https://orcid.org/0000-0002-3292-8845, e-mail: karataevage@mail.run

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