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Metallurgy



## Electrothermal processing of chrysotile-asbestos wastes with production of ferroalloy and extraction of magnesium into the gas phase

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### ABSTRACT

The article presents the results of an experimental study on the processing of wastes from chrysotile-asbestos production at Kostanay Minerals JSC. An electrothermal technology for the extraction of magnesium and siliceous ferroalloy from the chrysotile-asbestos wastes is proposed. The influence of the amount of coke and steel shavings on the technological parameters of the obtained alloys is determined. The results of derivatographic and SEM analyses of the chrysotile-asbestos waste samples are presented. The studies included planning experiments using the second-order rotatable designs (Box-Hunter plans), graphical optimization of technological parameters, and electric melting of a charge in a graphite crucible using a single-electrode arc furnace. Adequate regression equations were obtained explaining the effect of the amount of coke and steel shavings added to the chrysotile-asbestos waste on the extraction degree of silicon into the alloy and the silicon concentration in the alloy. By the electric melting of the charge, high-quality FS25 grade ferrosilicon with a silicon content of 24.4-29.2% and FS45 grade ferrosilicon with a silicon content of 41.6-45% were obtained. It was established that FS45 grade ferrosilicon with the extraction degree of silicon into the alloy from 75 to 85.4% is formed in the presence of 33.6-38% of coke and 16-20.8% of steel shavings. FS25 grade ferrosilicon is formed in the presence of 30-38% of coke and 29.4-40% of steel shavings; the extraction degree of silicon is 68.6-73.8%.

**Keywords:** chrysotile-asbestos waste, coke, steel shavings, rotatable planning, electric smelting, arc furnace, ferrosilicon

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### Introduction

Kazakhstan is among the top three leaders in the world in the extraction and processing of chrysotile ores. In accordance with [1], the Zhetikara deposit located in the Kostanay region ranks fifth in the world in terms of chrysotile-asbestos reserves. Chrysotile-asbestos production from ores of this deposit is organized at Kostanay Minerals JSC. Up to 5 million tons of chrysotile-

asbestos are extracted annually at Kostanay Minerals JSC [2].

When enriching 1 ton of the chrysotile-asbestos ore by the dry gravity method [3], 0.92 tons of wastes are formed, which contain 39.45-40.25% of MgO, 36.0-38.67% of SiO<sub>2</sub>, 2.8-4.89% of Fe<sub>2</sub>O<sub>3</sub>, 1.98-3.18% of FeO, 1.03-1.31% of Al<sub>2</sub>O<sub>3</sub>, 0.16-0.24% of NiO, 0.025-0.77% of Cr<sub>2</sub>O<sub>3</sub>, 0.75-1.96% of CaO, 0.3-0.46% of CO<sub>2</sub>, 0.12-0.48 of SO<sub>3</sub>, 11.48-13.67% of loss on ignition, 0.1-0.15% of others (TiO<sub>2</sub>, MnO,

K<sub>2</sub>O, Na<sub>2</sub>O) [[4], [5], [6]]. Thus, the main components in the wastes are MgO and SiO<sub>2</sub> [[7], [8], [9]]. 1.16 million tons of magnesium, 0.73 million tons of silicon, and 9.0 thousand tons of nickel are annually lost at Kostanay Minerals JSC. There are some methods of chrysotile-asbestos waste processing using acid leaching [[10], [11]]. The disadvantage of these methods is their multi-stage. For example, according to [10], the production of magnesium from serpentinite includes grinding the waste, leaching with HCl, separating the solution from the precipitate, purifying and concentrating the solution, obtaining synthetic carnallite, its multi-stage dehydration to obtain magnesium chloride raw materials for electrolysis, electrolysis to obtain magnesium and chlorine. We propose an electrothermal technology for magnesium and siliceous ferroalloy production from chrysotile-asbestos wastes with fewer stages compared to the hydrometallurgical method.

**Initial materials. Research Methodology**

According to [[12], [13]], chrysotile-asbestos wastes contain serpentine (3MgO\*2SiO<sub>2</sub>\*2H<sub>2</sub>O) – 57%, talc (3MgO\*4SiO<sub>2</sub>\*H<sub>2</sub>O) – 17%, brucite (Mg(OH)<sub>2</sub>) – 9%, forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) – 6-7%, magnesium, and iron oxides (MgO, FeO, Fe<sub>2</sub>O<sub>3</sub>) – 8-9%. DTA and SEM analyses of a chrysotile-asbestos waste sample, performed with using a derivatograph Q-1500D (DEMO) and a scanning electron microscope, are shown in Figures 1 and 2.

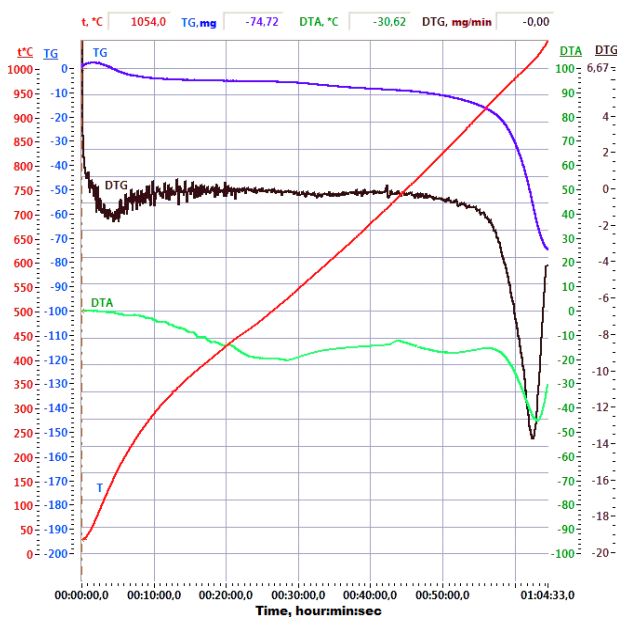
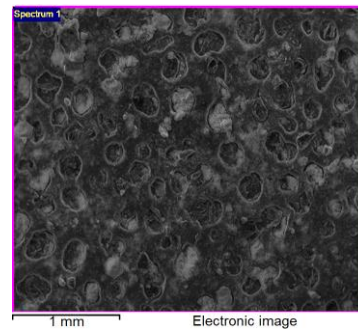
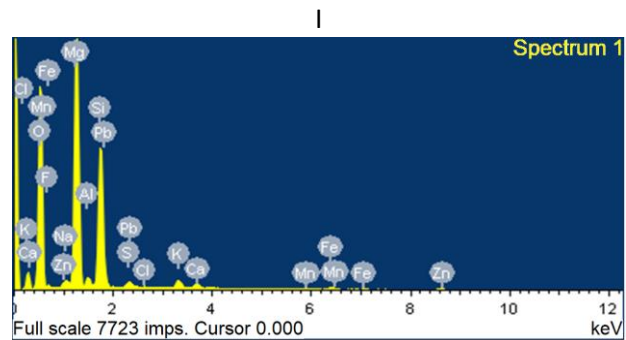


Figure 1 – Derivatogram of the chrysotile-asbestos waste

It is seen that the weight loss of the chrysotile-asbestos waste is 12.5%. According to the SEM analysis, the initial waste sample contained 46.0% of MgO, 35.8% of SiO<sub>2</sub>, 2.4% of Al<sub>2</sub>O<sub>3</sub>, 0.9% of Na<sub>2</sub>O, 1.5% of K<sub>2</sub>O, 0.9% of CaO, 1.2% of Fe<sub>2</sub>O<sub>3</sub>, 1.4% of ZnO, 1.0% of PbO, 0.3% of MnO, 10% of others. For melting, the chrysotile-asbestos waste sample was used calcined at 800°C for 30 minutes; its composition was 50% of MgO, 38.9% of SiO<sub>2</sub>, 2.7% of Al<sub>2</sub>O<sub>3</sub>, 1% of Na<sub>2</sub>O, 1.6% of K<sub>2</sub>O, 1% of CaO, 1.3% of Fe<sub>2</sub>O<sub>3</sub>, 1.5% of ZnO, 1.1% of PbO, 0.3% of NiO, and 0.1% of Cr<sub>2</sub>O<sub>3</sub>. Coke was used produced on the West Siberian Metallurgical Plant and contained 88.2% of solid carbon, 1.5% of volatiles, 1.2% of S, 9.1% of ash (including 4.5% of SiO<sub>2</sub>, 2.3% of Al<sub>2</sub>O<sub>3</sub>, 1.5% of Fe<sub>2</sub>O<sub>3</sub>, 0.5 of ∑ (CaO and MgO), 0.1% of others. Steel shavings contained 98.2% of Fe, 1.1% of C, 0.3% of Si, 0.2% of Mn, and 0.2% of others.

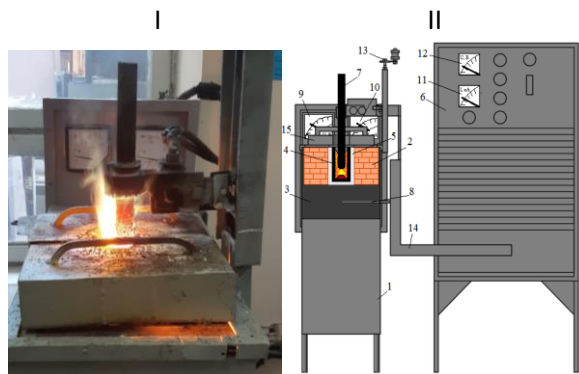


Element	O	F	Na	Mg	Al	Si	S
Weight %	46.63	1.25	0.74	27.61	1.25	16.77	0.6
Element	Cl	K	Ca	Mn	Fe	Zn	Pb
Weight %	0.15	1.22	0.64	0.27	0.85	1.1	0.93

I - spectrogram, II - elemental composition

Figure 2- SEM analysis of the chrysotile-asbestos waste

The studies included electric melting using a single-electrode arc furnace, shown in Figure 3.



1 – furnace shell, 2 – chromium-magnesite lining, 3 – coal-graphite hearth, 4 – graphite crucible, 5 – coal-graphite layer, 6 – transformer TDZF-1002, 7 – graphite electrode, 8 – lower current lead, 9-12 – control ammeters and voltmeters, 13 – electrode movement mechanism, 14 – flexible part of a low-voltage circuit, 15 – furnace cover  
I – melting the charge, II – furnace with transformer

**Figure 3** – Single-electrode arc furnace

The electric melting of the charge was carried out in a single-electrode arc furnace (up to 15 kVA power) lined with chromium-magnesite bricks. The bottom electrode was made of a graphite block. A graphite crucible (d = 6 cm, h = 12 cm) was placed on the hearth. The furnace in the upper part was closed with a removable cover with holes for placing a graphite electrode with a diameter of 3 cm and a gas outlet. The crucible was preliminarily heated by electric arc for 20-25 min. After that, the first portion of the charge (200-250 g) was loaded into the crucible. It was melted for 3-6 minutes. Then, every 4-6 minutes, 200-250 g portions of the charge were loaded in the crucible. During 1 experiment, 1500-2000 g of the charge was melted. Occasionally, the temperature at the outlet of gases from the furnace was measured with a GM2200 pyrometer and the temperature of the outer graphite crucible surface at the reaction zone level was measured with a tungsten-rhenium thermocouple. The temperature under the furnace cover during the melting period was 900-1050°C, and the temperature by the crucible wall was 1750-1850°C. During the melting period, the current strength was 350-400A, and the voltage was 30-35V. Electricity was supplied to the furnace from transformer TDZF-1002. The required power was maintained by a thyristor regulator. After the electric melting, the furnace was cooled for 6-7 hours. The graphite crucible was removed from the

furnace and broken. The resulting ferroalloy was weighed and analyzed by the atomic absorption method on the AAS-1 instrument (Germany) to determine the metals' content. The ferroalloy density was determined by the pycnometer method according to [14]. Then, based on the density according to [15], the silicon content in the alloy was determined. Some alloys were analyzed by means of a scanning microscope (ASS-1N).

To determine the optimal parameters of the process, the second-order rotatable designs (Box-Hunter plans) were used [16]. To establish the regression equations for changing the optimization parameters, the technique [17] was used, and to construct the volumetric and horizontal images of the optimization parameters, the technique [18] was used. The optimal parameters were determined by combining the horizontal images in one figure. This method was described by us in articles [[19], [20], [21], [22]].

### Research results

Table 1 shows the planning matrix and research results. During the research, the effect of the coke (K) and steel shavings (St) amount (in % of the chrysotile-asbestos waste weight) on the extraction degree of silicon into the alloy ( $\alpha_{Si}$ ) and the silicon concentration in the alloy ( $C_{Si}$ , %) was studied.

**Table 1** – Planning matrix and research results

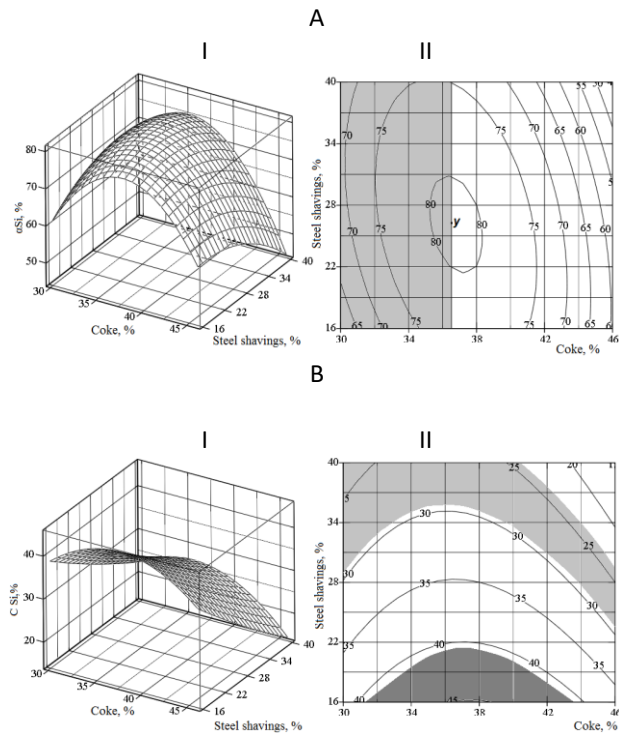
№	Variables				Technological parameters	
	Coded view		Natural view		$C_{Si}, \%$	$\alpha_{Si}, \%$
	X1	X2	Coke, %	Steel shavings, %		
1	+	+	43.7	36.5	21.0	56.6
2	-	+	32.3	36.5	26.3	70.9
3	+	-	43.7	19.5	37.0	69.3
4	-	-	32.3	19.5	39.0	73.0
5	1.41	0	46	28	25.6	57.9
6	-	0	30	28	30.8	69.7
7	0	1.41	38	40	27.5	78.0
8	0	-1.41	38	16	45.3	76.2
9	0	0	38	28	34.3	79.5
10	0	0	38	28	35.0	79.8
11	0	0	38	28	34.6	80.0
12	0	0	38	28	35.4	80.4
13	0	0	38	28	35.8	80.6

Using the data from Table 1, we found the regression equations according to the method [17]:

$$\alpha_{Si} = -361.43 + 22.47 \cdot K + 3.6 \cdot St - 0.272 \cdot K^2 - 0.03 \cdot St^2 + 3.6 \cdot K \cdot St; \tag{1}$$

$$C_{Si} = -1313.17 + 8.999 \cdot K - 0.392 \cdot St - 0.116 \cdot K^2 + 0.004 \cdot St^2 - 0.017 \cdot K \cdot St. \tag{2}$$

Based on equations 1 and 2, according to [18], the volumetric and horizontal images of  $\alpha_{Si}$  and  $C_{Si(ally)}$  were constructed (Figure 4).



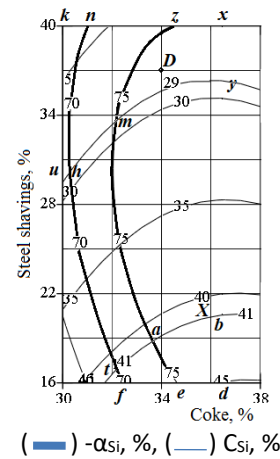
I - volumetric image, II - planar image

**Figure 4** – Effect of coke and steel shavings on the extraction degree of silicon into the alloy (A) and the silicon concentration in the alloy (B)

It can be seen that the surface of  $\alpha_{Si(ally)} = f(K, St)$  has an extremal view with a maximum ( $\alpha_{Si}=84.5\%$ ) at 37.0% of coke and 26.5% of steel shavings. The extremal view of the surface is due to the fact that at 36-38% excess coke (when  $\alpha_{Si(ally)}$  decreases), the electrical conductivity of the furnace bath increases. To maintain the required current, the electrodes together with the arc are moved to the upper horizons of the bath. The reaction zone also moves up. The throat is heated, and the filter layer of the charge decreases. As a result, the loss of silicon with gaseous SiO increases and  $\alpha_{Si(ally)}$  decreases. It is seen that  $\alpha_{Si}$  varies from 45 to 84.5% (x and y points).  $\alpha_{Si(ally)}$  from 64.6 to 84.5% is achieved at 30-37.0% of coke and 30-40% of steel shavings (shaded area of Figure 4

(I)). The silicon concentration in the alloy varies from 23.4 to 45.1%. FS45 grade ferrosilicon was formed at a small amount (<22%) of steel shavings in a large range of coke (from 32 to 42.5% of coke (shaded area of Figure 4 (II)). In the case of 30-46% of coke and and increased amount of steel shavings (from 23 to 40%), FS25 grade ferrosilicon was formed (shaded area of Figure 4 (B)).

To determine the optimal conditions, the planar  $\alpha_{Si}$  and  $C_{Si}$  images were combined (Figure 5). The values of technological parameters at the boundary points of the obtained ferroalloys are shown in Table 2.



**Figure 5** – Combined information about  $\alpha_{Si}$  and  $C_{Si}$

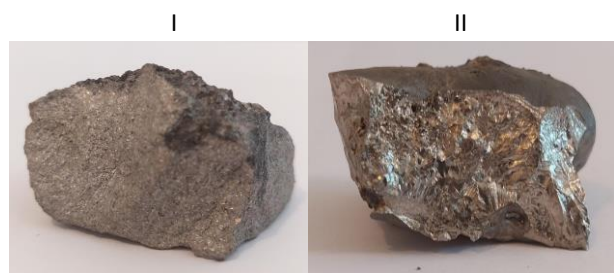
**Table 2** – Technological parameters at the points of Figure 5

Point in Figure 5	Technological parameter			
	Coke, %	Steel shavings, %	$\alpha_{Si}$ , %	$C_{Si}$ , %
t	32.3	16.8	70.0	41.0
a	33.6	18.7	75.0	41.0
b	38.0	20.6	79.0	41.0
d	38.0	16.0	76.6	45.0
e	34.4	16.0	75.0	44.7
f	32.5	16.0	70.0	41.4
u	30.0	29.4	69.4	29.0
K	30.0	40.0	68.6	32.4
n	30.9	40.0	70.0	34.1
z	34.4	40.0	75.3	25.9
x	36.2	40.0	75.0	25.4
y	36.2	35.6	76.7	29.0
m	32.2	32.5	75.0	29.0
h	30.3	30.4	70.0	29.0

In view of the fact that when the amount of coke is >36-38%, the right side of the Figure 5 surface is practically the same as the left (with a large amount of coke), it is advisable to consider the left side of the figure.

Based on Figure 5 and Table 2, it is possible to determine the optimal technological parameters for obtaining ferrosilicon of FS45 and FS25 grades [23] with different extraction of Si into the alloy. So, for  $\alpha_{Si} \geq 75\%$ , FS45 with  $C_{Si} = 41-45\%$  is formed in the region *abde* (33.69-36.2% of coke and 16-20.8% of steel shavings). For  $\alpha_{Si}$  from 70 to 75%, FS45 ferrosilicon with  $C_{Si} = 41-44.7\%$  is formed in the region *ftac* at 32.3-34.4% of coke and 16-18.7% of steel shavings. FS25 ferrosilicon with  $\alpha_{Si}(\text{alloy}) \geq 75\%$  and  $C_{Si} = 26.7-29\%$  is formed in the region *mzxy* at 32.2-38% of coke and 32.5-40% of steel shavings. FS25 ferrosilicon is also formed in the region *hnzm*. However, in this area,  $\alpha_{Si}$  decreases to 70%. In this case, the amount of coke can be changed from 30.3 to 34.4% and the number of steel shavings from 30.4 to 40%.

Figure 6 shows the ferroalloys obtained from two charge compositions: 1<sup>st</sup> charge – 58% of chrysotile waste, 22% of steel shavings, and 20% of coke; 2<sup>nd</sup> charge – 63% of chrysotile waste, 23% of coke, and 14% of steel shavings.



I – ferroalloy obtained from the 1<sup>st</sup> charge, II – ferroalloy obtained from the 2<sup>nd</sup> charge

Figure 6 – Photos of resulting ferroalloys

The silicon content in the alloy was determined based on its density ( $P$ , g/cm<sup>3</sup>) by the pycnometric method according to the equation:

$$C_{Si} = 252.405 - 101.849 \cdot P + 18.209 \cdot P^2 - 1.213 \cdot P^3 [15] \quad (3)$$

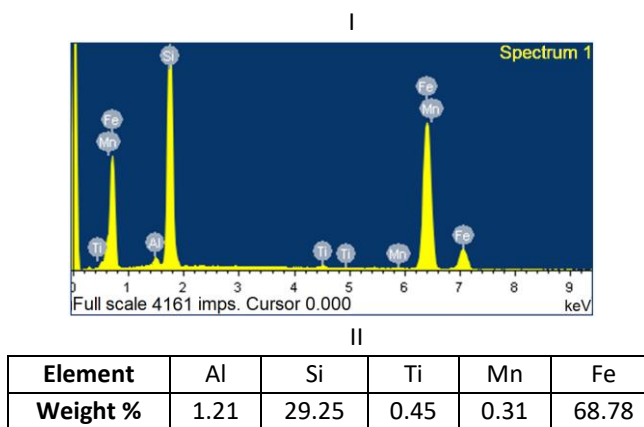
Density of the first ferroalloy was 6.4 g/cm<sup>3</sup>, and density of the second one – 5.47 g/cm<sup>3</sup>. The silicon content in the first alloy was:

$$C_{Si} = 252.405 - 101.849 \cdot 6.4 + 18.209 \cdot 6.4^2 - 1.213 \cdot 6.4^3 = 24.4\% \quad (4)$$

and in the second alloy:

$$C_{Si} = 252.405 - 101.849 \cdot 5.47 + 18.209 \cdot 5.47^2 - 1.213 \cdot 5.47^3 = 41.6\% \quad (5)$$

The SEM analysis of the first alloy is represented in Figure 7.



I - spectrogram, II - elemental composition

Figure 7 – SEM-analysis of the alloy

It is seen that the alloy produced from the first charge composition contains 29.2% of silicon. Judging by the silicon content, in accordance with [23], the produced alloys correspond to ferrosilicon of FS25 and FS45 grades. The obtained ferroalloys do not contain magnesium. The extraction degree of magnesium into the gas phase was at least 92-98%. The rest of magnesium (2-8%) passed into the slag. For the condensation of magnesium from the gas phase, it is recommended to use the Magneterm method [24].

### Conclusion

The results obtained during the electric melting of chrysotile-asbestos waste allow us to draw the following conclusions:

- FS45 grade ferrosilicon with the silicon extraction degree from 75 to 85.4% is formed in the presence of 33.6-38% of coke and 16-20.8% of steel shavings;
- FS25 grade ferrosilicon with the silicon extraction degree from 68.6 to 73.8% is formed in the presence of 30-38% of coke and 29.4-40% of steel shavings;
- the main amount of magnesium (92-98%) passes into the gas phase; the resulting ferroalloys do not contain magnesium.

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## Ферроқорытпа алу және газ фазасына магний алу арқылы хризотил-асбест өндірісінің қалдықтарын электротермиялық өңдеу

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<sup>2</sup>Қазақстан Республикасының минералдық шикізатты кешенді қайта өңдеу жөніндегі ұлттық орталығы, Алматы, Қазақстан

<p>Мақала келді: 23 қараша 2022 Сараптамадан өтті: 24 қаңтар 2023 Қабылданды: 22 ақпан 2023</p>	<p><b>ТҮЙІНДЕМЕ</b></p> <p>Мақалада «Қостанай минералдары» АҚ хризотил-асбест өндірісінің қалдықтарын қайта өңдеу бойынша эксперименттік зерттеулердің нәтижелері келтірілген. Хризотил-асбест өндірісінің қалдықтарынан магний мен кремнийлі ферроқорытпаны алудың электротермиялық технологиясы ұсынылды. Алынған қорытпалардың технологиялық параметрлеріне кокс пен болат жоңқалары мөлшерінің әсері анықталды. Хризотил-асбест өндірісінің қалдықтарын талдаудың дериватограмма мен растрлық электронды микроскопиясы ұсынылған. Зерттеулер екінші ретті айналмалы жоспарларды (Бокс-Хантер жоспары) қолдана отырып, эксперименттерді жоспарлау әдісімен жүргізілді, технологиялық параметрлерді графикалық оңтайландыру және бір электродты доғалы пешті қолдана отырып, графитті тигельде электр балқыту. Хризотил-асбест қалдықтарының массасынан кремнийді қорытпаға алу дәрежесіне және кремний қорытпасындағы концентрацияға кокс пен болат жоңқалары мөлшерінің әсер етуінің барабар регрессия теңдеулері алынды. Шихтаны электрмен балқыту арқылы құрамында 24,4-29,2% кремнийі бар ФС25 маркалы сұрыпты ферросилиций және 41,6-45% кремнийі бар ФС45 маркалы ферросилиций алынды. ФС45 маркалы Ферросилиций оған өту дәрежесі 75-тен 85,4% - ға дейін Si 33,6-38% кокс және 16-20,8% болат жоңқаларының қатысуымен түзіледі. ФС25 маркалы Ферросилиций, оған өту дәрежесі 68,6-73,8% кремний 30-38% кокс және 29,4-40% болат жоңқалары кезінде түзіледі.</p> <p><b>Түйін сөздер:</b> хризотил-асбест қалдықтары, кокс, болат жоңқалары, айналмалы жоспарлау, электр балқыту, доға пеші, ферросилиций</p>
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## Электротермическая переработка отходов хризотил-асбестового производства с получением ферросплава и извлечением магния в газовую фазу

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**АННОТАЦИЯ**

В статье приводятся результаты экспериментальных исследования по переработке отходов хризотил-асбестового производства АО «Костанайские минералы». Предложена электротермическая технология извлечения магния и кремнистого ферросплава из отходов хризотил-асбестового производства. Определены влияние количества кокса и стальной стружки на технологические параметры полученных сплавов. Представлены дериватограмма и растровая электронная микроскопия анализа проб отходов хризотил-асбестового производства. Исследования проводились методом планирования экспериментов с использованием рототабельных планов второго порядка (план Бокса-Хантера) с исследующей графической оптимизацией технологических параметров и электроплавкой шихты в графитовом тигле с использованием одноэлектродной дуговой печи. Получены адекватные уравнения регрессий влияния количества кокса и стальной стружки от массы хризотил-асбестовых отходов на степень извлечения кремния в сплав и концентрацию в сплаве кремния. Электроплавкой шихты получен сортовой ферросилиций марок ФС25 с содержанием кремния 24,4-29,2% и ФС45 с содержанием кремния 41,6-45%. Ферросилиций марки ФС45 со степенью перехода в него от 75 до 85,4% Si образуется в присутствии 33,6-38% кокса и 16-20,8% стальной стружки. Ферросилиций марки ФС25 со степенью перехода в него 68,6-73,8% кремния образуется при 30-38% кокса и 29,4-40% стальной стружки.

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