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# Complex electrothermal processing of an oxide zinc-containing ore of the Shaymerden deposit

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Abstract: Oxide ores are potential world raw materials sources of zinc manufacture. Despite a sufficiently high extraction level of zinc and lead known pyrometallurgical methods are characterized by formation of large quantity of industrial wastes therefore a complex use level of these raw materials is low. Hydrometallurgical methods are mainly applied for extraction of nonferrous metals. The present article contains the research results of complex processing an oxide ore of the Shaymerden deposit (Kazakhstan), consisting in the simultaneous production of a ferroalloy, calcium carbide and zinc sublimates from the ore in a thermal-ore arc electric furnace. The researches have been carried out with use of a HSC 5.1 software package (based on a principle of Gibbs energy minimum) and electrical smelting the ore in a monoelectrode arc electric controlled-output furnace. It was found, that in equilibrium conditions in a system ore-carbon-iron gaseous zinc is formed at T > 1073 K, FeSi at T > 1573 K, CaC<sub>2</sub> at T > 2073 K, Si at T > 1673 K. The electrosmelting of ore in an arc furnace using of 38.7-40 % coke and 16-28.4% steel cuttings the conversion degree of silicon into an alloy is 75-77%, calcium to calcium carbide 77-81%, zinc to sublimates 99.3%. The ferroalloy obtained contains 19.6-41.3% of silicon, the calcium carbide is characterized by capacity of 110-250 m<sup>3</sup>/kg, and the zinc sublimates contain 66-67% of zinc. The -suggested method allows to increase the combined usage of the ore from 35.6 to 89.6%.

Keywords: electrosmelting, zinc-containing oxide ore, calcium carbide, ferroalloy, zinc sublimates.

# 1. Introduction

According to the US Geological Survey data (The global commodity markets, 2015) world available zinc resources make 250 Tg. Zinc is mainly as a sulphide. In spite of the fact that zinc is generally produced from sulphide ores, a potential raw resource of zinc manufacture is oxide ores (5-7 % from the general reserves (Shevko and Karataeva, 2015), which are in Kazakhstan (Achisay, Shaymerden, Shalkiya, Zhayrem), the USA (Mississippi), Bulgaria (Sedmochislentsy), and Poland (Bytom, Olkush) (Methodical recommendations on application «Lead and zinc ore», 2007). For example, in Kazakhstan, which zinc reserves make 37.1 % (Shevko and Karataeva, 2015), oxide ores contain not less than 1.8 Tg zinc. Now oxide zinc ores are processed by flotation and also pyro- and hydrometallurgical methods. Production of flotation concentrates includes preliminary sulfidizing of oxide minerals by copper sulphate, sodium sulfide (Abramov, 2005; Algebraistova and Kondrateva, 2009), pyrite concentrate (Chanturia and Trofimov, 1985; Antropova et al., 2009; Gulyashinov et al., 2003; Antropova, 2005). Despite practical use of this method to Australia and a possibility to extract into a concentrate to 90 % of zinc (Kazanbaev et al., 2007), this method is characterised by formation of large-tonnage wastes such as flotation tails. Hydrometallurgical ways of processing oxide zinc ores are based on leaching zinc by various solvents (Kazanbaev et al., 2007; The production of heavy non-ferrous metals, 1974; Kim et al., 2010; Klebanov et al., 1974; Napo et al., 2011; Mamyachenkov et al., 2016; Irannajad et al., 2013; Qin et al., 2003; Ma et al., 2016; Aichun, 2016) (mainly by a sulfuric acid solution) (Kazanbaev et al., 2007; The production of heavy

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non-ferrous metals, 1974; Kim et al., 2010; Klebanov et al., 1974; Napo et al., 2011; Mamyachenkov et al., 2016). In spite of the fact that the hydrometallurgical methods allow us to extract into solutions to 98 % of zinc, they are connected with formation of a waste cake with which, as well as with the concentration tails, calcium, silicon and iron are lost.

Among pyrometallurgical ways of processing oxide ores, such as distillation in retorts, shaft and electric furnaces and Waelz processing, the Waelz process has the greatest use. It is done in the presence of coke at 1523-1573 K in revolving furnaces. Despite the extraction of 88 % of zinc and 90 % of lead in sublimates (Abdeev et al., 1985), constant reduction of coke consumption, increase in productivity of the furnaces, and increase of extraction degree of metals in sublimates (Kozlov et al., 2008; Gizatulin et al., 2006; Kazanbaev et al., 1998) this method is characterized by high duration (2.5-3 hours), high coke consumption (45-55 % of the ore weight), and formation of a waste clinker (0.85-0.95 Mg per 1 Mg of the ore) with which 15-30 % of carbon and practically all iron, silicon and calcium are lost. Therefore, the extraction level of the ore in the Waelz processing is low.

On the basis of the above-mentioned information we can say that the problem of non-waste processing oxide ores has not been solved yet. The presented article contains results of our researches connected with the complex processing of oxide zinc ores of the Shaymerden deposit (zinc reserves are 0.927 Tg) (Palenova et al., 2010; Minerals and deposits of Russia and CIS countries, 2015) by combining in one furnace three processes: obtaining a silicon ferroalloy, calcium carbide and oxide zinc sublimates.

## 2. Materials and methods

At implementation of the research we have used a thermodynamic modelling technique and experimental electrosmelting the ore in an electric arc furnace.

Thermodynamic modelling of obtaining a ferroalloy, calcium carbide and gaseous zinc out of the ore has been carried out on a base of a HSC 5.1 software package developed by a Finnish metallurgical company Outokumpu (nowadays Outotec) (Roine, 2002). Calculation of equilibrium by the HSC 5.1 program is realized on the basis of a Gibbs energy minimum principle taking into consideration activities of substances (a subprogram Equilibrium Compositions). Developers of the HSC 5.1 software package have based on an ideology of a SGTE consortium (Scientific Group Thermodata Europe, 2018) which develops, supports and distributes high-quality databases intended for calculation of an equilibrium composition of chemically reacting systems. The SGTE structure includes specialized scientific centers in Germany, Canada, France, Sweden, the Great Britain and the USA (Scientific Group Thermodata Europe, 2018). Error of the calculations by the HSC 5.1 program is no more than 2-4%.

Electrosmelting a charge containing the zinc ore has been performed in a monoelectrode arc furnace lined with chrome-magnesite bricks. A hearth-level electrode was made from a graphite slab. A graphite crucible (d = 6 cm, h = 12 cm) was placed on the bottom. Space between the crucible and the lining was filled with broken graphite. The furnace in the top part was covered with a removable cover with apertures for a graphite electrode (d = 3 cm) and gas discharge. The atmosphere in the furnace was air. Furnace gases through a dust chamber were removed by a fan. In the chamber there was partial sedimentation of zinc-containing sublimates. Before the electrosmelting the crucible was heated by means of electric arc within 20-25 minutes. The first portion of a charge (200 g) was loaded into the crucible after the heating. It melted during 5-6 minutes, then the remaining charge (200 g) was also loaded and melted within 25-30 minutes. Current during the smelting was 250 - 300 A, and voltage was 45-50V. A transformer TDZhF-1002 was used for supply of electricity in the furnace. Necessary power has been supported by a thyristor regulator. Control of current strength was done by an ammeter Tangen 42L6 (error percentage 1,5%) and voltage by a voltmeter Chint 42L6 (error percentage 1,5%). After the electrosmelting the furnace was cooled within 6 hours. The graphite crucible was taken from the furnace and broken. The carbide and ferroalloy formed were weighed and analyzed for determination of Zn, Fe, Si and Ca content.

The analysis of raw materials, ferroalloys and sublimates were done with use of a scanning electronic microscope (SEM) JSM-6490LM (Japan), and atomic adsorption technique with ASS-IN (Germany). The analysis error of the SEM is <1 %, and AAS-IN <0.3 %). Content of the elements in the analyzed substance has been determined as mean value of three analyses. Content of  $CaC_2$  in the obtained technical calcium carbide ( $C_{CaC_2}$ , %) has been calculated under the formula (Kozlov and Lavrov, 2011):

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

where L is the calcium carbide capacity ( $m^3/kg$ ), a volume of the acetylene formed at decomposition of the calcium carbide by water according to the reaction  $CaC_2 + H_2O = C_2H_2 + Ca(OH)_2$ , 372 is quantity of  $m^3$  of the acetylene formed at decomposition of 1 kg of 100 % calcium carbide at 293 K and pressure of 101.325 kPa.

Calcium carbide capacity is a qualitative characteristic determined experimentally (Kozlov and Lavrov, 2011). It is calculated using the formula (2):

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

where p and  $p_1$  are atmospheric pressure and water steam tension during the experiment (mm·Hg), V is volume of the acetylene formed (cm³), G is calcium carbide weight (g), t is temperature (K), L is calcium carbide capacity (m³/kg). The experimental error is no more than 1-1.5%.

Besides the SEM analysis the silicon content in the alloy ( $C_{Si}$ , %) has been determined in accordance with its density (D,  $g/cm^3$ ). The density has been measured by a pycnometer with application of kerosene. Calculation of  $C_{Si}$  has been implemented according to the preliminary obtained formulae (3) and (4) (Shevko et al., 2016):

$$C_{\text{si}} = 690.679 - 545.783 \times D + 166.151 \times D^2 - 17.467 \times D^3 (D = 3.52 - 6.09g/cm^3);$$
 (3)

$$C_{Si} = 130.878 - 21.232 \times D + 0.859 \times D^2 (D = 6.09 - 7.859g/cm^3).$$
 (4)

In this case the error of  $C_{Si}$  determination is no more than 2 %.

The experimental extraction degree of calcium from the charge into technical calcium carbide has been calculated under the formula (5):

$$\alpha_{Ca(cc)} = \frac{G_{cc} \times C_{CaC_2} \times \frac{MCa}{MCaC_2}}{G_{ore} \times C_{Ca(ore)} + G_{coke} \times C_{Ca(coke)}} \times 100,$$
(5)

where  $G_{ore}$ ,  $G_{coke}$  and  $G_{cc}$  are masses of the ore, coke and technical calcium carbide (kg),  $C_{Ca(ore)}$  and  $C_{Ca(coke)}$  are calcium content in the ore and the coke (%),  $C_{CaC2}$  is  $CaC_2$  content in the technical calcium carbide (%),  $M_{Ca}$  and  $M_{CaC2}$  are calcium atomic weight and calcium carbide molecular.

The extraction degree of silicon from the charge into the ferroalloy has been calculated according to the expression (6):

$$\alpha_{Si(cnnae)} = \frac{G_{alloy} \times G_{Si}}{G_{ore} \times C_{Si(ore)} + G_{coke} \times C_{Si(coke)}} \times 100;$$
(6)

where  $G_{alloy}$  is the ferroalloy mass (kg),  $C_{Si(ore)}$  and  $C_{Si(coke)}$  are silicon concentration in the ore and the coke (%),  $C_{Si}$  is silicon concentration in the alloy (%).

The experimental extraction degree of zinc and lead (Me) from the charge into sublimates has been calculated under the formula:

$$\alpha_{Me(subl)} = \frac{G_{ore} \times C_{Me(ore)} - G_{ocm} \times C_{Me(res)}}{G_{ore} \times C_{Me(ore)}} \times 100; \tag{7}$$

where  $C_{Me(ore)}$  is concentration of the metals (Zn, Pb) in the ore (%),  $C_{Me(res)}$  is concentration of the metals (Zn, Pb) in the solid residue formed after the decomposition of the technical calcium carbide by water (%),  $G_{res}$  is mass of the solid residue formed at the calcium carbide decomposition (kg).

In the calculation of Zn and Pb extraction into the sublimates their content in the alloy was left out because in the samples it did not exceed 0.0-0.01 %.

When thermodynamic modelling was done with HSC 5.1 software package the calculation of equilibrium distribution of the elements (Si, Ca, Zn) into other substances was done using the formula (8):

$$\alpha_{\text{element}} = \frac{G_{\text{element(init)}}}{G_{\text{element(form)}}} \times 100, \tag{8}$$

where  $G_{element(init)}$  is mass of an element (Si, Ca, Zn) in starting material (kg) and  $G_{element(form)}$  is mass of the element (Si, Ca, Zn) in the formed substance (kg).

The tests were done using ore containing 22.82-23.94 % Zn, 8.89-9.38 % Si, 11.11-11.37 % Ca, 2.22-2.40 % Fe, 0.54-0.65 % Pb (Fig.1 and Table1). The coke applied as a reducer contained 86.4 % C, 11.2 % ash, 1.3 % volatile substances, 0.8 % water and 0.3 % S. The steel cuttings composition was 98.2 % Fe, 0.3 % Si, 1.3 % C, and 0.2 % other species. The ore and coke particle sizes were 3-5 mm, and the steel cuttings 1-8 mm.

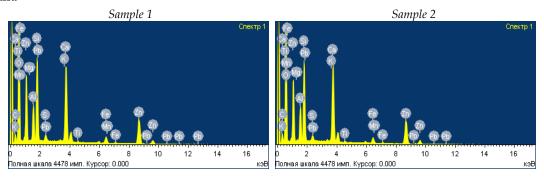


Fig. 1. Energy-dispersion spectra of the Shaymerden ore made by the scanning electron microscope

Table 1. The Shaymerden ore composition determined by the SEM

Content, %	С	O	Mg	Al	Si	S	K	Ca	Ti	Mn	Fe	Zn	Pb
Sample 1	5.94	40.27	0.34	4.47	9.38	0.56	0.16	11.11	0.30	0.45	2.40	23.94	0.65
Sample 2	7.72	40.23	0.36	4.35	8.89	0.56	0.22	11.37	0.24	0.49	2.22	22.82	0.54

#### 3. Results and discussion

By means of the HSC 5.1 program it was found out, that the basic components of the ore (ZnO, SiO<sub>2</sub>, CaO) at the presence of carbon and iron interact with each other, a main reaction:

$$ZnO + SiO_2 + CaO + Fe + 6C = Zn + FeSi + CaC_2 + 4CO;$$
 (9)

the interaction picture is represented in Fig. 2.

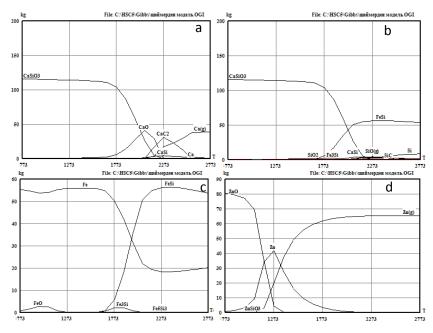


Fig. 2. Temperature effect on quantitative equilibrium distribution of the substances containing calcium, silicon, iron and zinc in a system of  $ZnO-CaO-SiO_2-Fe_2O_3-6C$  obtained by means of the HSC 5.1 software package (a - Ca, b - Si, c - Fe, d - Zn)

According to Fig. 2,  $Zn_{(gas)}$  is formed at  $T \ge 1073$  K, calcium carbide at  $T \ge 2073$  K, Si at  $T \ge 2073$  K and iron silicides at  $T \ge 1573$  K.

Fig. 3 shows the silicon equilibrium distribution ( $\alpha_{Si}$ , %) in the system Shaymerden ore – C (40 % of the ore mass) – Fe into basic silicon-containing compounds. On the assumption of the Fig. we can say that the increase in iron quantity from 17 % to 31 % of the ore weight raises  $\alpha_{Si}$  in FeSi, and reduces it in SiC, SiO<sub>(gas)</sub> and elemental Si. The total silicon transition in the alloy as FeSi, Si, CaSi, Fe<sub>5</sub>Si<sub>3</sub> is represented in Table 2. Silicon concentration in the alloy decreases from 47 to 26%.

The temperature dependence of  $\alpha_{Ca}$  in the CaC<sub>2</sub> has maximum at 2273 K. At T > 2273 K  $\alpha_{Ca}$  in the CaC<sub>2</sub> decreases in connection with the calcium carbide decomposition: CaC<sub>2</sub> = Ca + 2C (Ershov et al., 1974). It leads to decrease of the calcium carbide capacity and its quality loss. Increase of the iron content (Fe, % of the ore mass) in the system brings to reduction of  $\alpha_{Ca}$  in CaC<sub>2</sub> (fig.4) from 85.9 to 81.4% (at 2273K) according to the equation (10):

$$\alpha_{Ca}(CaC_2) = 82.372 + 0.4938 \cdot Fe - 1.69 \cdot 10^{-2} \cdot Fe^2$$
 (10)

In the process the calcium carbide capacity also decreases from 219-220 to 211-213 m $^3$ /kg (Fig. 4). Zinc distribution into  $Z_{(gas)}$  is not dependent on the iron quantity and is 97-99.9% at 1973-2473 K. Lead at 2273 K passes into a gaseous state by 85-89% (Fig. 5).

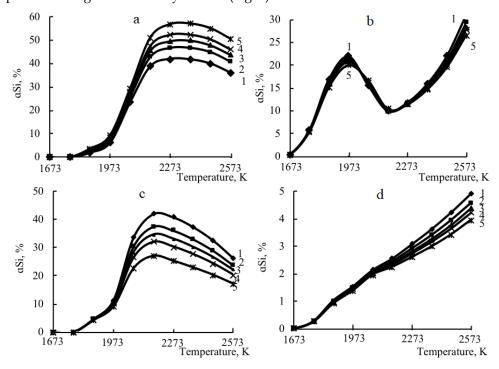


Fig. 3. Influence of temperature and iron content on  $\alpha Si$  in a system Shaymerden ore – iron – carbon calculated using HSC 5.1 software package. (a)  $\alpha Si$  in FeSi; (b)  $\alpha Si$  in Si; (c)  $\alpha Si$  in SiC; (d)  $\alpha Si$  in SiO<sub>(gas)</sub>, iron fractions 1 - 17% of Fe; 2 - 21% of Fe; 3 - 24% of Fe; 4 - 27% of Fe; 5 -31% of Fe

Table 2. Influence of temperature and iron amount on the equilibrium silicon distribution degree into the alloy and the silicon content in it calculated using HSC 5.1 software package.  $\alpha$ Si is Si extraction degree and  $\alpha$ Si is Si content in the alloy

F = 0/ = f = 1.1	Temperature, K									
Fe, % of ore weight	2073	2173	2273	2373	2473	2573				
17	αSi 41.2	aSi 49.7	aSi 53.9	aSi 57.8	aSi 64.4	aSi 66.9				
17	% Si 41.1	% Si 46.3	% Si 47.0	% Si 47.2	% Si 47.3	% Si 47.3				
24	aSi 44.3	aSi 54.9	aSi 64.1	αSi 66.0	aSi 68.8	αSi 73.4				
24	% Si 26.5	% Si 31.4	% Si 34.5	% Si 34.5	% Si 34.6	% Si 34.7				
21	aSi 48.3	aSi 64.8	aSi 70.5	αSi 74.5	aSi 75.9	αSi 77.9				
31	% Si 20.3	% Si 25.1	% Si 26.6	% Si 26.8	% Si 26.8	% Si 26.9				

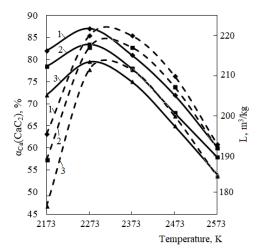


Fig. 4. Influence of temperature and iron quantity on the equilibrium Ca transition degree into  $CaC_2$  (%) and the calcium carbide capacity (L, m³/kg). (–) –  $\alpha$ Ca in  $CaC_2$ , %; (- -) – L, m³/kg. Iron fraction 1 – 17% of Fe; 2 – 24% of Fe; 3 – 31% of Fe

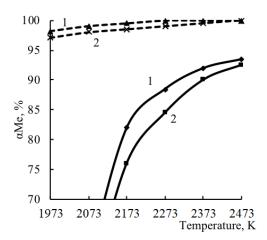


Fig. 5. Temperature effect on the zinc and lead equilibrium distribution degree in a gas phase. (-) -  $\alpha$ Pb into Pb<sub>(gas)</sub>, %; (--) -  $\alpha$ Zn into Zn<sub>(gas)</sub>, %. Iron fraction 1 - 17% of Fe; 2 - 31% of Fe

Using a rotatable second-degree method of planning an experiment (similar to the Box-Behnken second-order Rotatable Design) (Akhnazarova and Kafarov, 1978), we have carried out 13 melts in an arc electric furnace with different amounts of steel cuttings (St, % of the ore weight) and coke (C, % of the ore weight) (Table 3). The following questions were studied: Influence of the steel cuttings and coke amounts on the silicon transition degree in the alloy ( $\alpha_{Si(alloy)}$ , %), calcium in calcium carbide ( $\alpha_{Ca(cc)}$ , %), silicon content in the alloy ( $\alpha_{Si}$ , %), the calcium carbide capacity ( $\alpha_{Si}$ , CaC<sub>2</sub> concentration in the carbide ( $\alpha_{CaC_2}$ ). The experimental results are represented in Table 3.

Using the data of Table 2 the following regression equations (10)-(14) have been obtained:

$$\alpha_{Si(alloy)} = 90.978 + 0.1287 \times St - 2.226 \times C + 0.002 \times St^2 + 0.0477 \times C^2 - 0.0126 \times St \times C; \tag{10}$$

$$C_{Si} = 80.404 - 1.42 \times St - 1.726 \times C + 0.0154 \times St^2 + 0.0315 \times C^2 - 0.005 \times St \times C; \tag{11}$$

$$\alpha_{CaC_2} = 173.873 - 0.95 \times St - 8.359 \times C - 2.029 \times 10^{-2} \times St^2 + 0.149 \times C^2 + 3.78 \times 10^{-2} \times St \times C; \quad (12)$$

$$C_{CaC_{s}} = 384.35 + 0.771 \times St - 22.663 \times C - 0.0218 \times St^{2} + 0.3898 \times C^{2} - 0.771 \times St \times C;$$
(13)

$$L = 1617.65 - 0.4623 \times St - 92.198 \times C - 0.048 \times St^{2} + 1.498 \times C^{2} - 0.1235 \times St \times C.$$
(14)

The  $\alpha_{Si(alloy)}$  and  $C_{Si}$  isolines in coke % vs. steel cuttings % coordinates have been constructed on the basis of these equations (Fig. 6).

# of		Variabl	e factors	i	~~~~ °/	C %	or 9/	$C_{cac_2}$ , %	I m3/lca	
	Coded		Uncoded		- asi(alloy), %	C <sub>Si(alloy)</sub> , %	α <sub>Ca(cc)</sub> , %	$CaC_2$	L, 1117/Kg	
	$X_1$	$X_2$	St, %	C, %						
1	-1	-1	19.5	31.5	67.9	32.4	54.6	32.5	128.5	
2	+1	-1	36.5	31.5	66.6	20.5	39.9	27.7	101.1	
3	-1	+1	19.5	38.5	73.4	33.9	75.3	54.86	198.1	
4	+1	+1	36.5	35.8	70.6	21.4	65.1	41.2	156	
5	1.41	0	40	35	67.6	19.5	47.3	31.2	118.1	
6	-1.41	0	16	35	71.9	37.6	66.6	47.6	168.5	
7	0	1.41	28	40	74.7	29.6	78.8	58.3	220.3	
8	0	-1.41	28	30	66.3	24.6	48.3	33.3	125.7	
9	0	0	28	35	69.1	25.8	59.1	32.9	127.7	
10	0	0	28	35	69.8	25.0	59.6	34.8	132.3	
11	0	0	28	35	68.5	26.6	59.7	34.2	126	
12	0	0	28	35	68.5	25.9	58.9	34.3	131.3	
13	0	0	28	35	69.5	26.4	58.3	36.2	133.6	

Table 3. The research matrix and the results of the Shaymerden ore electrosmelting

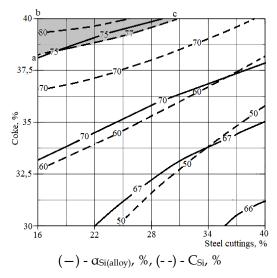


Fig. 6. Steel cuttings and coke concentration effect on the silicon extraction degree in the alloy and calcium in the carbide at the electrosmelting the Shaymerden ore

As follows from Fig. 6, high extraction of silicon in the alloy (75-77%) is observed in the area *abc* at 38.7-40 % of coke and 16-28.4 % of steel cuttings. At the same time the calcium extraction degree in the carbide makes 77-81 %, zinc in the sublimates 99.3 %, lead 99.1%. In this area silicon concentration in the alloy changes from 33 to 42 % (point b), and the calcium carbide capacity varies from 230 to 250 m<sup>3</sup>/kg (point b). Photographs of the alloys obtained at the smelting different charges are represented in Fig. 7, and a characteristic of the sublimates formed is shown in Fig. 8 and Table 4.



Fig. 7. Photographs of the obtained ferroalloys (fragments). 1 - 40% of C, 17% of St (41.3% of Si); 2 - 40% of C, 35% of St (27.4% of Si); 3 - 30% of C, 40% of St (19.6% of Si)

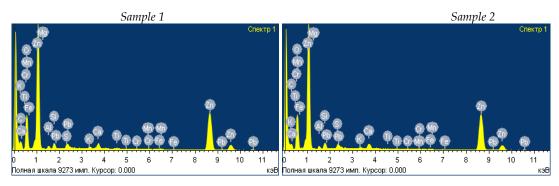


Fig. 8. Energy-dispersion spectra of the sublimates made on the scanning electron microscope

Table 4. Compositions of the sublimates determined by scanning electron microscope

Content, %	C	O	Mg	Al	Si	S	K	Ca	Ti	Cr	Mn	Fe	Zn	Pb
Sample 1	6.29	18.53	0.48	0.97	0.19	0.91	0.39	1.35	0.31	0.15	0.33	0.37	67.05	1.34
Sample 2	6.46	19.1	0.44	1.02	1.68	0.69	0.34	1.36	0.07	0.00	0.32	0.47	66.42	1.65

As is evident from Fig. 7, the ferroalloy with low silicon content is formed at a considerable quantity of steel cuttings. In this case the calcium carbide capacity decreases and its quality becomes worse. So, at 30% of coke the increase of steel cuttings quantity from 16 to 40% lowers the carbide capacity from 150 to  $110 \, \text{m}^3/\text{kg}$ . The sublimates obtained contain 66.42-67.05% of Zn and 1.54-1.65% of Pb, that is more than in industrial samples on 12-16% (Abdeev et al., 1985).

Unlike a Waelz process the suggested method of processing oxide zinc ores allows us to increase considerably a multipurpose use level of the ore ( $\gamma$ ) in terms of the basic elements (Si, Zn, Pb, Fe, Ca). So, at the Waelz processing this coefficient  $\gamma(w)$  makes (15)

$$\gamma(w) = \frac{\alpha_{Si(subl)} + \alpha_{Pb(subl)} + \alpha_{Si} + \alpha_{Ca} + \alpha_{Fe}}{5} \times 100 = \frac{87,8 + 90 + 0 + 0 + 0}{5} \times 100 = 35,6\%, \tag{15}$$

where  $\gamma(w)$  is multipurpose recovery level of the ore at the Waelz processing (%),  $\alpha_{\text{Zn(subl)}}$ ,  $\alpha_{\text{Pb(subl)}}$  are zinc and lead transition degrees into the sublimates at the Waelz processing (%),  $\alpha_{\text{Si}}$ ,  $\alpha_{\text{Ca}}$ ,  $\alpha_{\text{Fe}}$  are transition degrees of silicon, calcium and iron into the waste clinker at the Waelz processing (%).

For the suggested method the use level is (16)

$$\gamma(s) = \frac{\alpha_{Si(subl)} + \alpha_{Pb(subl)} + \alpha_{Si(alloy)} + \alpha_{Ca(carbide)} + \alpha_{Fe(alloy)}}{5} \times 100 = \frac{99.3 + 99.1 + 75 + 80 + 95}{5} \times 100 = 89.6\%$$
 (16)

where  $\gamma(s)$  is multipurpose use level of the ore for the suggested process (%),  $\alpha_{Zn(subl)}$ ,  $\alpha_{Pb(subl)}$  - zinc and lead extraction degrees into the sublimates (%),  $\alpha_{Si(alloy)}$ ,  $\alpha_{Fe(alloy)}$  are silicon and iron extraction degrees into the ferroalloy (%),  $\alpha_{Ca(carbide)}$  are calcium extraction degree into the carbide (%). Thereby, the suggested method makes it possible to increase a multipurpose recovery level of the ore in 2.5 times.

### 4. Conclusions

On the basis of the obtained results concerning the complex processing the Shaymerden oxide ore we can draw following conclusions. In equilibrium conditions in a system of the ore – carbon – iron  $Zn_{(gas)}$  is formed at T > 1073 K, FeSi at T > 1573 K,  $CaC_2$  at T > 2073 K, Si at T > 1673 K. Temperature effect on the calcium transition in  $CaC_2$  has maximum at 2273 K caused by the calcium carbide decomposition into calcium and carbon. The increase of iron quantity from 17 to 31 % of the ore mass leads to increase of the equilibrium silicon distribution in the alloy to 77.9 %, reduces the silicon distribution in SiC and  $SiO_{(gas)}$ , calcium in calcium carbide (from 85.9 to 81.4 %), slightly reduces the zinc and lead distribution in the sublimates (however, it remains sufficiently high: 99.6-99.9 % for zinc and 85-89 % for lead at 2273K), decreases the silicon content in the alloy from 47 to 26 % and the calcium carbide capacity from 220 to 213 m³/kg.

At the electrosmelting the ore in an arc furnace within 30-36 min in conditions of 38.7-40 % of coke and 16-28.4% of steel cuttings the silicon extraction degree in the alloy is 75-77 %, calcium in calcium

carbide 77-81%, zinc in sublimates 99.3%; the ferroalloy produced contains 19.6-41.3 % of silicon; the calcium carbide capacity is 110-250 m<sup>3</sup>/kg; zinc content in the zinc sublimates makes 66-67 %.

The suggested method enables to increase the ore multipurpose use level from 35.6 to 89.6%, i.e. in 2.5 times.

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## References

- ABDEEV M.A., KOLESNIKOV A.V., USHAKOV N.N., 1985, Wellawaya zinc lead-containing materials, Moscow: Metallurgy, 120p.
- ABRAMOV A.A., 2005, The technology of processing and concentration of red wet metals, Moscow, Publishing house of Moscow state University, volume 2, 470p.
- AICHUN D., 2016, A Novel Process for Treating with Low Grade Zinc Oxide Ores in Hydrometallurgy, TMS 2016: 145 Annual Meeting & Exhibition: Supplemental Proceedings.
- AKHNAZAROVA S.A., KAFAROV, B.V., 1978, Methods for optimization of experiment in chemical industry, Moscow: High school, 319p.
- ALGEBRAISTOVA N.K., KONDRATEVA A.A., 2009, Lab. workshop "The Technology of enrichment of ores of nonferrous metals", Krasnoyarsk: IATSFU, 80p.
- ANTROPOVA I.G., 2005, Physico-chemical and technological bases sulfidizing firing of oxidized lead zinc ore in the atmosphere of superheated steam, thesis of the candidate. tech. Sciences, Krasnoyarsk, 146p.
- ANTROPOVA I.G., GULYASHINOV A.N., LEMUEL V.A., PALEEV P.L., 2009, Method of processing of refractory oxidized lead ore, Patent Russian Federation #2364639.
- CHANTURIA, V.L., TROFIMOV E.A., 1985, Processing of oxidized ores, Moscow: Science, 69-71.
- ERSHOV V.A., DANCIS J.B., REUTOVICH L.N., 1974, *The production of calcium carbide*. Leningrad: Chemistry, 147p. GIZATULIN O.V., IVAKIN D.A., KAZANBAEV L.A., KOZLOV P.A., KOLESNIKOV A.V., 2006. *Charge for Waelz*
- zinc-containing materials, Patent Russian Federation #2284361.
- GULYASHINOV A.N. ANTROPOVA I.G. KALININ YU.O. HANTURGAEVA G.I, 2003, Method for processing of oxidized zinc ore, Patent Russian Federation #2208059
- IRANNAJAD M., MESHKINI M., AZADMEHR A., 2013, Leaching of zinc from low grade oxide ore using organic acid, Physicochemical Problems of Mineral Processing, #49(2), 547-555.
- KAZANBAEV L.A., KOZLOV P.A., KOLESNIKOV A.V., RESHETNIKOV YU.V., 1998, Method of rolling of oxidised zinc-containing materials, Patent Russian Federation #2119965.
- KAZANBAEV L.A., KOZLOV P.A., KUBASOV V.L., 2007, *Hydrometallurgy of zinc. The process of leaching*, Moscow: Ore and metals, 120p.
- KIM L.D., TULYAGANOV SH.R., MAMATKULOV H., VEJLIVCEV A.A., MAVLONKULOV R.K., CHOI YU.N., MAMATKULOV P.H., 2010, Method for processing poor oxidized zinc ores and concentrates with the recovery of zinc, manganese, iron, lead, silver, calcium and silicon dioxide, Patent Russian Federation #2441930.
- KLEBANOV O.B., SHUBOV L.Y., SHCHEGLOV N.K., 1974, Reference technologist for the enrichment of ores of non-ferrous metals, Moscow: The bowels, 319-323.
- KOZLOV K.B., LAVROV, B.A., 2011, *Obtaining calcium carbide in an arc furnace and its analysis*. Saint-Petersburg, Saint-Petersburg state technological Institute (technical University), 20p.
- KOZLOV P.A., KOLESNIKOV A.V., KONONOV A.I., MIZIN V.G., SAMSIKOV E.A., SPERKACH I.E., 2008, A method of processing Gelezinkeliai materials, Patent Russian Federation #2329312.
- MA A., PENG J., ZHANG L., SHIWEI L., YANG K., ZHENG X., 2016, Leaching Zn from the low grade zinc oxide ore in  $NH_3$   $H_3C_6H_5O_7$   $H_2O$  media, Brazilian Journal of Chemical Engineering, #33.
- MAMYACHENKOV S.V., RAMAZANOVA R.A., BYKOV R.A., SERAYA N.V., 2016, Evaluation of the process of sulfuric acid leaching of zinc from oxidized zinc ore truboobrabotka of the mathematical modeling, Complex Use of Mineral Raw Materials #3, 63-66.
- Methodical recommendations on application of Classification of reserves and prognostic resources of solid minerals «Lead and zinc ore», Moscow, 2007, 40p.

- Minerals and deposits of Russia and CIS countries: [Electronic resource]. URL: http://webmineral.ru/deposits/item.php?id=1533 (Date of access: 30.05.2015).
- NAPO D., NTULI F., MUZENDA E., MOLLAGEE M., 2011, *Process Intensification of Zinc Oxide Leaching Process Using Sulphuric Acid*, Proceedings of the World Congress on Engineering and Computer Science, #II, 5.
- New methods for processing zinc-containing raw materials abroad: review. inform. *The production of heavy non-ferrous metals*, Moscow: CRIEICM, rel. 1, 1974, 44p.
- PALENOVA E.E., BELOGUB E.V., KOTLYAROV V.A., 2010, Mineralogy of oxidized ores of the Deposit Shaimerden, Saint-petersburg: XI Congress of the pod. Modern Mineralogy: from theory to practice, 231-233.
- QIN W., LAN ZH., LI W., 2003, *Recovery of zinc from low grade zinc oxide ores by solvent extraction*, Journal of Central South University of Technology, #10, 98-102.
- ROINE A., 2002, Outokumpu HSC Chemistry for Windows. Chemical Reaction and Equilibrium loftware with Extensive Thermochemical Database, Pori: Outokumpu Research OY.
- Scientific Group Thermodata Europe: [Electronic resource]. URL:http://sgte.net/en/ (Date of access: 03.01.2018).
- SHEVKO V.M., AMANOV D.D., KARATAEVA G.E., AJTKULOV D.K., 2016, *Kinetics of receiving of complex Ferroalloy of silicon-aluminum-containing flasks*, International journal of applied and fundamental research, #10-2, 194-196.
- SHEVKO V.M., KARATAEVA G.E., 2015, *Metallurgy of zinc and cadmium*, Shymkent: South Kazakhstan State University, 350p.
- The global commodity markets: [Electronic resource]. URL:http://www.cmmarket.ru/ (Date of access: 18.05.2015).