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Complex processing of oxidized copper and zinc oxide ores with simultaneous production of several products

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Abstract: Modern production of non-ferrous metals is imperfect due to the loss of rock mass and metal in the technological chain ore mining to metal production. Processing of zinc oxide and oxidized copper ores by hydrometallurgical, pyrometallurgical and flotation methods is associated with formation of dump cakes, clinkers and flotation tailings. Therefore, all these methods are characterized by a low coefficient of complex use of raw materials (for example, for the Waelz process this coefficient is not higher than 35%). To increase the degree of complex processing of oxide raw materials, it is necessary to change the attitude to raw materials and create industrial technologies based on new principles. The article presents theoretical and applied research results on complex processing of oxidized copper and zinc oxide ores based on the new attitude to raw materials and new effective technologies allowing us to increase significantly the level of raw materials' complex processing. Theoretical regularities, features and optimal technological parameters of new methods of complex processing of oxide, zinc and oxidized copper ores were found based on the ideology of a universal technological raw material and the simultaneous production of several products in one furnace unit.

Keywords: zinc ores, copper ores, calcium carbide, ferroalloys, zinc sublimates

1. Introduction

Production of non-ferrous metals from sulfide, oxide and mixed raw materials is currently imperfect due to the loss of both the rock mass and the target metal in the process chain from the ore mining to the metal production in the form of overburden, off-balance ores, concentration tailings, slags, clinkers, cakes, dusts, slurries, waste water, and metal waste. Moreover, the amount of the waste increases exponentially (Zaicev, 2002).

A greater part of the ores used in non-ferrous (90%) and ferrous (85%) metallurgy is subjected to various types of concentration (Lykasov, 2010), which inevitably leads to formation of concentration tailings. The bulk of the ore is lost with the tailings. For example, at the flotation of 100 t of copper sulphide ore containing 0.5% copper in a case of extraction of 94% of copper into a 30% copper concentrate, the flotation tailings mass is 100-0.5·0,94/0,3=98.4 Mg. In Kazakhstan, only two processing plants (Dzhezkazgan and Balkhash) have accumulated about two billion tons of mineral raw materials in tailing dumps (Baimakova, 2002; Baibatsha, 2008). A certain amount of non-ferrous metals is then extracted from the tailings by various methods (Snurnikov, 1986), but the non-metallic part of the tailings is usually not used to produce a useful product. It is mainly applied for filling old mine workings and producing construction materials (Snurnikov, 1986; Lamani et al.,2016).

The metals' extraction degree from sulfide ores into final products is also characterized by low technological indicators. The degrees of copper extraction at application of different types of smelting are given in table 1 (Kazhikenova, 2010).

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The table shows that only 81.0% (Noranda)-88.4% (Outokumpy) of copper can be extracted from the ore to the metal. Analysis of lead production by different ways (shaft melting, melting in liquid bath, hearth melting, and the OSCET process (oxygen suspended cyclone electro thermal process) in accordance with (Kazhikenova, 2010) shows that the transition degree of lead to the metal is from 75.9% (mine melting) to 83.3% (melting in a liquid bath).

Table 1. The copper extraction degree into cathode copper

Melting type	Extraction degree, %					
	From the ore into concentrate	From the concentrate into matte	From the matte into crude copper	From crude copper into anode copper	From anode copper into cathode copper	From the ore into cathode copper
Melting in liquid bath	96.1	97.3	94.7	98.1	99.99	81.9
Oxygen torch melting	92.1	96.2	93.8	98.2		81.6
Noranda	93.3	97.4	93.2	95.6		81.0
Outokumpy	97.7	98.7	93.2	98.4		88.4
Mitsubishi	92.3	97.1	92.8	98.6		82.0
Suspended melting	95.2	97.4	94.3	98.3		85.9

The situation with the processing of oxide and oxidized ores is no better. Now the world copper reserves amount to 635 Tg (Brief overview of the world market for copper,2020*)*. The copper content in oxidized and mixed copper minerals in these ores is about 10% (Methodological recommendations, 2007*)*; it is 635·0.1 = 63.5 Tg. Information about the reserves of copper oxidized ores in Kazakhstan is not available in the literature. Bearing in mind that the Kazakhstan copper reserves are 33-41 Tg (Smirnov, 2010; Date views, 2020), it can be indirectly assumed that the reserves of copper containing in Kazakhstan oxidized and mixed ores are from 33*0.1=3.3 Tg to 41*0.1=4.1 Tg. Taking into account that the average copper content in the ores is 0.5%, its reserves in Kazakhstan are approximately from 660 to 820 Tg. These oxidized ores can be concentrated using flotation or leaching (in-situ, heap, or vat ways).

By the end of the last century, several methods of concentrating oxide and mixed copper-containing ores were known (Bekturganov and Abishev, 1989). Flotation concentration of oxidized and mixed copper-containing ores includes preliminary activation of the oxide minerals with chelating reagents (8-oxyquinoline, salicylaldoxime, α-benzosim, benztriazole, alkylbenztriazole) and subsequent flotation of the resulting copper-containing complexes with amyl xanthogenate. Effective flotation reagents for the oxide ores containing chrysocolla are also phenylpseudothiohydantoin, hydroxamic acids. Anti-5-ionyl-2-hydroxybenzophenolxime can form stable water-insoluble chelate compounds on the surface of copper oxide minerals. In the process, it is possible to extract 91% of the copper. α-alkylthioacetophonoxime also has high flotation activity in respect towards the copper oxide minerals. Tertiary phosphine and quaternary phosphonic dinitrates, oxyhydrazine compounds, β-diketones, and salicylaldoximes are also used for flotation of copper oxide ores. However, these reagents are expensive and they have been tested either for only a few ore samples, or for artificial materials. To improve the flotation of copper oxide ores, their preliminary sulfidation is carried out in various variants (Bayeshov and Dospayev, 1990; Bekturganov and Omarov,1990; Omarov,1996; Sycheva et al., 2003; Bakov and Arzhannokov, 2000; Zhumashev et al., 2009; Panova and Yeliseyev, 1994).

The most common hydrometallurgical method for extracting copper from hard-to-recover oxidized ores is heap leaching (Lamani et al.,2016). In this case, convention al leaching agents are sulfuric acid and sulfuric acid solutions of divalent and trivalent iron. Solutions after the leaching are processed by cementation with iron scrap (Kreyn, 2004) or extraction followed by electrolysis (SX-EW process) (Vladimirov and Mihailov, 1976; Yun, 2013). Leaching of copper from oxidized ores has been developed in a number of countries (Chile, the USA, Australia and Peru) (Fazlullina, 2005; Mark et al., 2011; Aksenov et al., 2014). In Kazakhstan, the sulfuric acid heap leaching technique was tested on almost 30 types of oxidized and mixed ores (Research Institute of non-ferrous metals) (Kushakova and Sizikova, 2018; Kushakova, 2008). The enriched productive solutions are processed with two mixtures: 2E-W-1S (two extraction stages, water washing, one re-extraction) and 2E-Ep-W-1S (two stages and one parallel stage including extraction, water washing, re-extraction). The following extra gents are used: Lix 984N, Lix84-1, Acorda M5640, Mextral. The technology including leaching, solvent extraction and electrolysis is applied now in Kazakhstan to process ores of such deposits as Aktogay (annual production capacity is 25 ths Mg of cathode copper), Kounrad, Shatyrkul, Ayak-Kojan and ready-to-use field Almaly.

Heap leaching, which provides a high degree of copper extraction from the ore, however, does not solve the problem of its complex processing. It is focused on extracting only the base metal – copper. At the same time, the plenty of wastes remains on the ground surface, polluting the environment.

Zinc oxide and oxidized ores are processed by three methods: concentration, hydrometallurgical and pyrometallurgical ones.

Flotation of these ores is performed in the presence of aliphatic amines and sodium sulfide (Glembockii and Anfimova, 1966). This method was used at some processing plants (Galetti, Buggerru, Sartoria, Mauda, Agruxo, San Giovanni) (Abramov, 1986). According to the Andreyeva-Davis method, at the Rizo factory, the mixed ore after sulfidation is activated with copper vitriol. Then it is floated with amine or isoaminexanthogenate and dithiophosphate (Glembockii and Anfimova, 1966). The degree of zinc recovery in a 35-37% zinc concentrate is 75%.

Recently, several new methods of concentration of zinc oxide ores have been proposed: sulfidizing roasting in the atmosphere of superheated water vapor in the presence of a pyrite concentrate (Gulyashinov et al., 2003); depressing of limestone and dolomite with citric acid, and silicates and iron oxides with liquid glass and caustic soda when flotation of ordinary smithsonite ores with extraction of 83.6% Zn into a concentrate containing 43.5% zinc (Algebraistova and Kondrat'yeva, 2009); depressing a rich zinc ore with sodium fluoride and dextrin using cationic and cationic-ion collectors (KAX-Armac with a ratio of 2:1) (Mehdilo et al.,2013). However, despite the obvious success of flotation enrichment of oxide ores, known and new methods are associated with the inevitable formation of tailings.

Zinc hydrometallurgy is based on leaching of the ore with different acid and alkali solutions (Yoshida Takashi, 2003; Ai-yuan et al., 2016; Irannajad et al., 2013). Research in this area is conducted in South Africa, Japan, China, Iran, Turkey, and Kazakhstan. Processes of leaching zinc oxide ores are widely applied by American Smelting and Refining Company, Corpus Christi, TX; Anaconda Company, MT; Consolidated Mining and Smelting Company of Canada Ltd., Trail, B.C; Bunker Hill Company, Kellogg, ID; Electrolytic Zinc Company of Australasia, Risdon, Tasmania; Hudson Bay Mining and Smelting Company, FlinFlon, Manitoba (Gupta and Mukherjee, 1990). However, all these processes, despite the high zinc extraction degree (90-98%), are associated with the formation of a dump cake. The only exception is the work (Kim et al., 2012), which provides extraction of zinc, manganese, iron, lead, silver, calcium, and silicon from zinc oxide ores. However, due to a large number of stages, long duration and lack of information about transition of the metals in products, this method cannot be classified as a promising one.

The Waelz process is the main pyrometallurgical method for processing oxide ores (Romanteyev et al., 2006). Despite the extraction of 88-90% of Zn and Pb from the ores and a number of technological improvements (Mizin et al., 2008; Kazanbayev et al., 1998; Kazanbayev et al., 2006; Shevko, 1992a), the main disadvantages of the Waelz process are a significant consumption of coke (45-55% of the ore weight), long duration (2-3 hours) and formation of a waste product – clinker (85-89% of the charge weight) that leads to loss up to 15-30% of the coke.

The present article contains the research results obtained at South Kazakhstan State University in the end of the XXth – the beginning of the XXIst centuries on the processing of hard-to-enrichoxide and oxidized zinc and copper ores on the basis of the ideology about a universal technological raw material, and one of the ideology principles is simultaneous joint production of several products (target and intermediate ones)in one furnace unit (Shevko and Aitkulov, 2019a; Shevko and Aitkulov, 2019b). In our case, intermediate products are artificial raw materials that are used to produce new products. Variants for implementing the technology are shown in Fig. 1.

2. Research methodology

The thermodynamic modeling was carried out using the HSC-5.1 (Roine, 2002) and Astra (Sinyarev and Vatolin, 1982) software packages based on the principles of minimum Gibbs energy and maximum

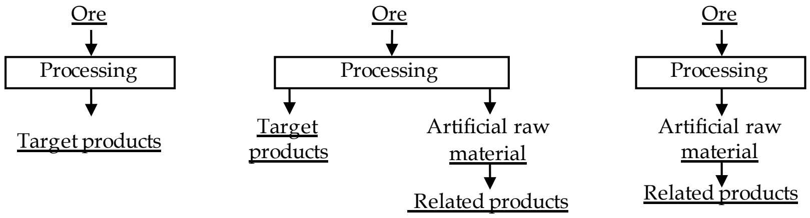


Fig. 1. Variants of schemes for processing zinc and copper oxide raw materials with simultaneous production of target products, artificial raw materials and related products

entropy, respectively. When using the HSC-5.1 software package, the Reaction Equations module was applied to calculate ΔG_T^0, and the Equilibrium Compositions module was used to determine the equilibrium quantitative distribution of substances (kg). The equilibrium element distribution degree was calculated using the algorithm developed by us and protected by copyright (Shevko et al., 2019d). The absolute error of these studies did not exceed 2-3%.

Most of the experiments and the final stage of the thermodynamic analysis were implemented using second-order rotatable Box-Hunter designs (Akhnazarova and Kafarov, 1978). The results of the experiments carried out according to the matrix were used to obtain regression equations for the influence of independent factors on the technological parameters – optimization parameters. The error in determining the adequacy of the equations does not exceed 5%. Then, according to the technique (Ochkov, 2007) and using a computer, we constructed volumetric and planar images (indicating the optimization parameter values on the lines) of the influence of independent factors (temperature, pressure, time, weights of the raw materials), on the basis of which thermodynamic optimization was carried out. This method allows us to determine the optimal parameters by superimposing several horizontal images on top of each other.

Experiments on the chloride sublimation of metals from ores were carried out using a granulated charge consisting of an ore and calcium chloride at a setup including a vertical electric furnace, a quartz reactor, an air compressor, a rheometer, a pressure gauge, a thermocouple with a millivoltmeter, and a sublimate catching system. The cinders, formed after the roasting, were analyzed to determine the content of non-ferrous metals and iron by the atomic adsorption method using an AAS-1 device (Germany).

The metals' chloridosublimation degree (αMe,%) was calculated by the formula:

$$a_{Me} = \frac{G_{ch} - G_c}{G_{ch}} \cdot 100 \quad (1)$$

where G_{ch} and G_c – the charge and cinder weights; $C_{Me(ch)}$ and $C_{Me(c)}$ – concentration of a metal in the charge and in the cinder, unit fraction. The absolute error of the experiments did not exceed 2-4%.

Studying the extraction kinetics of silicon into a ferroalloy, calcium into calcium carbide, and zinc into sublimates were performed in a Tamman furnace. The temperature was controlled by means of a VR-5/20 thermocouple. To determine the temperature in a crucible, the relationship between it (an OPIR-17 pyrometer) and the temperature in the lower part of the furnace (thermocouple VR-5/20) was previously found. A graphite crucible with a charge was put into the furnace (on a graphite support) and kept in it for a certain time. Then the crucible crossbeam was hooked with a steel hook and the crusible was removed from the furnace. The crucible was cooled and broken. The products formed during the melting the charge in the Tamman furnace were weighed and analyzed to determine the silicon and non-ferrous metals content in the ferroalloy and the CaC_2 content in the calcium carbide. The silicon content in the alloy (C_{Si}) was determined through its density (ρ) (Shevko et al., 2016) by the formulas:

- the density from 2.33 to 3.52 g/cm³

$$C_{Si}=690.679-545,783 \cdot \rho+166.151 \cdot \rho^2-17.467 \cdot \rho^3 \quad (2)$$

- the density from 3.52 to 6.09 g/cm³:

$$C_{Si}=130,878-2,232 \cdot \rho +0,859 \cdot \rho^2 \quad (3)$$

- the density from 6.09 to 7.859 g/cm³:

$$C_{Si}=3755.875-1.524 \cdot \rho +208.0 \cdot \rho^2-9.515 \cdot \rho^3 \quad (4)$$

The zinc content in the alloy and the calcium carbide was determined using a JSC-6490LV scanning electron microscope (Japan). The CaC_2 content in the calcium carbide was found through its capacity under the formula:

$$C_{CaC_2} = \left(\frac{L}{372}\right) \cdot 100 \tag{5}$$

where 372 – the volume of acetylene (l) released during the decomposition of 1 kg of pure calcium carbide with water at 20°C and a pressure of 760 mm Hg; L – the calcium carbide capacity determined according to the St. Petersburg Technological Institute (Technical University) method (Kozlov and Lavrov, 2011). The Ca extraction degree into calcium carbide (α_{Ca},%) was calculated by the formula:

$$\alpha_{Ca} = \frac{\left[C_{CaC_2} \cdot \frac{A_{Ca}}{M_{CaC_2}}\right] \cdot G_{ch}}{C_{Ca} \cdot G_{ch}} \cdot 100 \tag{6}$$

where C_{Ca} and C_{CaC2}– the Ca concentration in the charge and the CaC_2 concentration in the calcium carbide, respectively, %; G_{ch} and G_{CC} – weights of the charge and calcium carbide, respectively.

The extraction degree of zinc into sublimates was determined by the following way:

$$a_{Zn(g)} = \frac{G_{ore} \cdot C_{Zn(ore)} - G_{alloy} \cdot C_{Zn(alloy)} - G_{CC} \cdot C_{Zn(CC)}}{G_{ore} \cdot C_{Zn(ore)}} \tag{7}$$

where G_{ore}, G_{alloy}, G_{cc} – weights of the ore, the alloy, the calcium carbide, g; $C_{Zn(ore)}$, $C_{Zn(alloy)}$, $C_{Zn(cc)}$ – Zn content in the ore, the alloy and the calcium carbide. The absolute error of this series of experiments did not exceed 4-5%.

The ores were electrosmelted in a single-electrode electric furnace. Before melting the charge, the graphite crucible (d = 6 cm, h = 15 cm) was heated by an arc ignited between the graphite electrode (d = 3.5 cm) and the bottom of the graphite crucible installed on the graphite support. The voltage to the electric furnace was supplied from a TDZhF-1002 transformer with a terristor power regulator from 5 to 40 kVA. When melting the charge (350-500 g), the current ranged from 300 to 400 A at a voltage of 20-30 V. After the end of the melting, the electrode was raised, the crucible was removed from the furnace and broken. The products formed during the melting the charge were weighed and analyzed: the ferroalloy was analyzed on the content of Si and non-ferrous metals, calcium carbide on the content of CaC_2, Zn, Pb according to the previously described technique.

Industrial tests were carried out at a semi-industrial unit of RPF Kazkhiminvest LLP (Taraz). A furnace unit is a single-phase electric furnace equipped with a 120 kV*A transformer of the OS-100/0.5-UHL4 type with three steps on its low side: I step (I = 2000A, U = 18-49 V), II step (I = 4000A, U = 18-9.2-24.5 V), III step (I = 8000A, U = 4.6-12.3 V). The voltage is supplied from the transformer to the electric furnace through the bottom electrode and a round graphite electrode with a diameter of 0.25 m. The bottom electrode is a self-sintering carbon-graphite block reinforced with an iron mesh.

The electric furnace lining is made of chromium-magnesia bricks. The electric furnace bath has the shape of a reverse truncated cone; its diameter in the lower part is 0.35 m, in the upper part is 0.75 m. The bath height is 0.65 m. The bath volume is 0.15 m^3, the area of the hearth is 0.0907 m^2. The furnace lining and hearth were encased. Voltage to the upper graphite electrode was supplied through a short network consisting of aluminum busbars and flexible cables. The electrode is moved by means of a mechanical mechanism. A metal mold is installed in the lower part of the hearth to drain slag, calcium carbide and ferroalloy. To transport the mold from the niche for cooling, the furnace is equipped with an inclined rack. The temperature at the top of the exhaust gases is measured by a PP-1 thermocouple paired with a millivoltmeter, and the temperature of the outlet melt (occasionally) – by a VR thermocouple. The gases from the electric furnace through an inclined gas duct in the roof of the furnace are fed into a dust chamber in which 3-8% of sublimates are deposited; then they are fed along a gas duct to gas coolers. The quantity of the sublimates precipitated in the coolers is no more than 30-40% of their total quantity. The gas temperature after the coolers is 160-220°C. For more accurate maintenance of the gas temperature at the inlet to bag filters, cold (outside) air is sucked in locality of them. The gas is cooled in the cooler using outside air to a temperature of about 110-115°C. Catching the sublimates occurs during the last stage of dust collection and fine gas purification in bag filters. The gases from the bag filters purified by means of an exhauster are released into the atmosphere. Methods of the products analysis and determination of metal extraction degrees have been described previously.

The absolute error of the experiments did not exceed 6%.

3. Experimental part

3.1. Processing of zinc-containing oxidized siliceous ores to produce ferrosilicon and zinc sublimates

The material provided in this section has been published by us in (Shevko et al.,2008; Shevko et al.,2009a; Shevko et al., 2009b; Shevko et al.,2009c; Shevko et al.,2010; Kapsalyamov and Shevko, 2008; Kapsalyamov et al.,2007). The Zhairem ore refers to carbonate ores; it contains 3-6% of ZnO, 0.3-0.4% of Pb, and, in addition, 42-75% of SiO_2, 2-3% of CaO, 0.5-0.7% of MgO, 5-7% of Fe_2O_3, 8-9% of Al_2O_3 and small quantities of manganese, barium, titanium, sodium and potassium oxides. The Shalkiya ore is a mixed ore with an oxidation degree of 80-90%. It contains 42-57% of SiO_2, 12-14% of Al_2O_3, 2.5-3.5% of ZnO, up to 0.1% of ZnS, 2.5-3.5% of CaO, 1.2-1.6% of MgO, 18-20% of Fe_2O_3, up to 0.4% of FeS_2. The ore also contains 3-6 g/t of silver, 0.05 g/t of gold, $6.9 \cdot 10^{-4}$% of germanium, potassium (up to 0.7%), titanium (up to 0.2%), sodium (up to 0.4%), manganese (up to 0.3%).

Silicon, zinc and iron oxides can simultaneously be reduced with carbon to produce zinc and iron silicides according to the reactions:

$$ZnO+2SiO_2+Fe_2O_3+8C=Zn_g+2FeSi+8CO; \quad (8)$$

$$ZnO+4SiO_2+Fe_2O_3+12C=Zn_g+2FeSi_2+12CO. \quad (9)$$

From the thermodynamic point of view, these reactions become probable at T≥1086 ^{0}C and T≥1290 ^{0}C, respectively. Using a thermodynamic modeling technique, the temperature and pressure effect on the zinc sublimation degree from the Zhayrem ore was found (Fig. 2). As follows from the figure, to achieve the 90-100% zinc sublimation level, the process must be carried out in the temperature range of 1320-1500 K and the pressure of 0.001-0.016 MPa. The kinetics of zinc sublimation is shown in Fig. 3. To achieve the zinc sublimation degree higher than 95%, the process should be realized for 15-60 minutes at 1973-1773K.

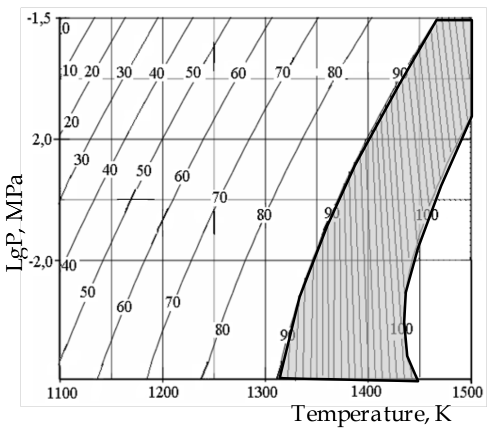


Fig. 2. Temperature and pressure effect on the Zn sublimation degree from the Zhayrem ore (the numbers on the lines – Zn sublimation degree, %)

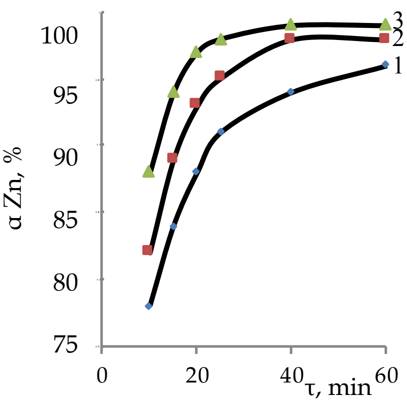


Fig. 3. Temperature and time effect on the Zn sublimation degree from the Zhayrem ore (1 – 1773K, 2 – 1873K, 3 – 1973K)

Using the experimental results obtained at the electrical smelting the Zhayrem ore (the average SiO_2 content is 42-47%) in an arc furnace and the Box-Hunter second-order design of experiments, a regression equation was found for determination of influence of steel shavings (St), Ekibastuz coal (C) and coke (K) amounts on the silicon content in the resulting ferroalloy:

$$C_{Si}=34.51-0.91St-3.21K+0.69C+0.023St^2+0.29K^2-0.047\cdot St\cdot K-0,016\cdot St\cdot C+0.083\cdot K\cdot C \quad (10)$$

On the basis of the equation a curve $C_{Si} = f(C, K)$ was constructed for a constant amount of steel shavings. The curve for 18% of steel shavings is represented in Fig. 4.

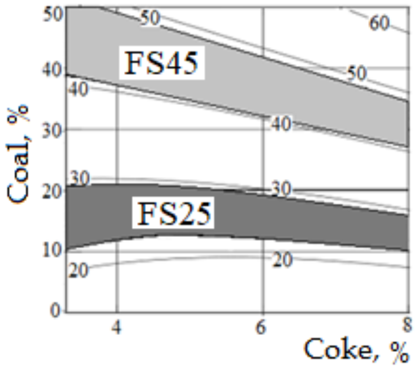
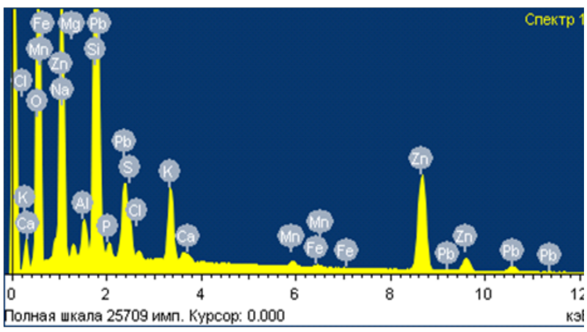


Fig. 4. The effect of coke and coal amounts on the silicon content in the ferroalloy (the numbers on the lines – Si content in the ferroalloy)

Fig. 4 shows that the resulting alloy can be classified as a ferroalloy of the FS25 and FS45 grades. A stable electrical mode is observed when obtaining the FS25-grade ferroalloy. It became somewhat worse when producing the FS45-grade ferroalloy. While trying to produce the FS65-grade ferroalloy, the Si transition degree in the alloy decreased to 40-50%. The Zn sublimation degree was 99.4-99.6%, and the lead one – 98.0%. The electric smelting of the Zhayrem ore with a high SiO_2 content (72-76%) occurs in a stable electric regime with formation of the FS45 ferroalloy.

It was established that the ferrosilicon of FS20, FS25 and FS45grades can be also produced from the ore of the Shalkiya deposit (1.6-2% of Zn, 1.4-1.8% of Pb, 42-44% of SiO_2). In this case the transition degree of Zn to the gas phase was 99.0-99.8%, and for lead - up to 99.6%. Trial electric melting of oxidized zinc ores with catching zinc sublimates in coolers and bag filters was carried out in production conditions at "Kazhiminvest" (Taraz, Kazakhstan). 2.5 Mg of Shalkiya ore and 1.0 Mg of Zhayrem ore were melted. During the electric smelting of the Shalkiya ore, the extraction degree of silicon in the alloy was 89.3%, iron 97.3% and the degree of zinc extraction in the sublimates was 99.7%. The resulting ferroalloy contained 24-43% of Si, the sublimates – up to 60-65% of ZnO. The electric power consumption per 1 Mg of the ferroalloy varied from 3,100 to 4,820 kWh. The electric smelting of the Zhayrem ore allowed us to extract 80.5% of Si and 96.5% of Fe in the alloy; 99.7% of Zn and 99% of Pb were extracted into the sublimates. The ferroalloy contained 20.6-42.6% of Si, the Zn content in the sublimates was 51-53% (Fig. 5). In addition to Si and Fe, the alloy contained 0,01% of Ge, 0,15% of Ti, 0,5% of C, 0,7% of V, 0,01% of W, 0,005% of Re, and also <0,001% of La, Pr, Hf, Ir, Os.



Element	Weight,%	Element	Weight,%
Na	2,81	Mn	0,45
Mg	0,54	Fe	0,15
Al	1,01	Zn	52,77
Si	7,47	Pb	6,08
K	2,04	O	24,88
Ca	0,27	Others	1,53

Fig. 5. Analysis of zinc sublimates produced from the Zhayrem ore (energy-dispersion spectra and sublimate composition made by the scanning electron microscope)

During the electric melting, the major part of calcium, aluminum, titanium (>90-95%) passes into slag, 3-5% into an alloy, the rest into a gas phase. The main part of manganese and chromium (70-90%) is extracted into a ferroalloy. 50-70% of titanium is also extracted into an alloy. The resulting slag is sold to enterprises as broken stone.

The electric energy consumption per 1Mg of the ferroalloy ranged from 3000 to 4780 kWh depending on its grade. The data obtained during the experimental smelting of Shalkiya ore allowed us to establish a fundamental relationship between the useful power of the furnace (P_{use}) and the useful voltage (U_{use}): U_{use} =12.43 $\cdot P_{use}{}^{0,25}$; this ratio permits to choose the optimal useful voltage.

Based on the pilot tests, we collectively with "Taraz metallurgical plant" LLP have developed the specification for the ferrosilicon produced of Shalkiya and Zhayrem zinc oxide ores.

The coefficient of complex use of the oxidized ore for the developed technology for the main elements (Zn, Si, Fe) is:

$$\gamma=(99.7(Zn)+80.5(Si)+96.5(Fe))/3=92.2\% \quad (11)$$

During processing of similar ores by the leaching this coefficient is only:

$$\gamma=(95(Zn)+0(Si)+0(Fe))/3=31.7\% \quad (12)$$

3.2. Processing of oxidized siliceous zinc-containing ores to produce a zinc concentrate and expanded clay

The material of this section has been published by us in (Shevko et al.,1989; Shevko et al.,1995; Shevko and Mel'nik, 1993; Shevko and Mel'nik, 1991a; Shevko and Takezhanov, 1989; Shevko, 1988; Shevko and Niyazbekova, 1994; Shevko, 1992b). The significant content of $\sum SiO_2$ and Al_2O_3 (50-90%) in the Zhayrem ore was the basis for development of a new technology for its processing, which provides production of expanded clay and zinc chloride sublimates in a single furnace unit (a rotating furnace).

The theoretical basis of this process has been developed. So, to determine the possibility of chlorination of metals with salts according to the reaction MeO+Me'Cl_2=MeCl_2+Me'O, we calculated the thermodynamic exchange criterion (K) as: $\left(\Delta G^0_{T_{MeCl_2}} - \Delta G^0_{T_{MeO}}\right) - \left(\Delta G^0_{T_{Me/Cl_2}} - \Delta G^0_{T_{Me/O}}\right) = K_{Me} - K_{Me'}$. The condition for the left-to-right reaction is the expression: $K_{Me} < K_{Me'}$. So, for example, at the temperature of 1400^{0}C, the K_i has the following values:

Table 2. K_i values at the temperature of 1400^{0}C

Element	Pb	Cu	Zn	Al	Ca	Fe(III)	Na	H
K_i	-14.9	-11.9	-8.8	9.7	-14.4	-0.1	-44.8	-3,3

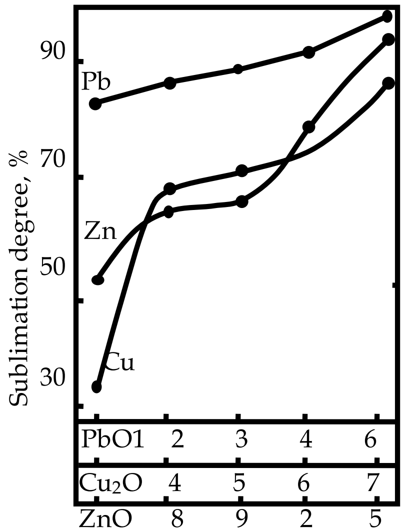
Based on the K_i values, under the equilibrium conditions, PbO can be chlorinated with $AlCl_3$, $FeCl_3$, HCl, $ZnCl_2$, $CuCl_2$ and $CaCl_2$. ZnO is chlorinated with $FeCl_3$, HCl, and CuO – with $AlCl_3$, $FeCl_3$, HCl, and $ZnCl_2$.

The study of the kinetics of non-ferrous metal chloride sublimation allowed us to determine the effect of various additives on the Cu, Zn and Pb chloride sublimation degree (Fig. 6), and this permitted to determine combinations of oxide additives accelerating the metals' chloride sublimation at constant temperature and time.

The acceleration of the chloride sublimation of Zn from ZnO occurs in the following line: PbO+Cu_2O+Fe_2O_3, PbO+Cu_2O, Cu_2O+Fe_2O_3, PbO+Fe_2O_3.

In relation to the Zhayrem carbonate ore, it was found that the chloride sublimation of Zn from $ZnCO_3$ proceeds more intensively and with a lower activation energy than from ZnO. It was established that the "carbonate" ZnO has an excess enthalpy of 3.4 kJ/mol caused by increasing the structure defect; it leads to the intensification of sublimation of Zn from $ZnCO_3$ and a decrease in the beginning Zn chlorination temperature by 65 ^{0}C. The interaction of ZnO with the $CaCl_2$ melt, which can dissociate forming $CaCl^+$ and Cl^-, occurs with the formation of an intermediate complex [ZnO...Cl]. The complex type and charge were determined experimentally – by means of calculating on the basis of the absolute entropy of the activated complex equal to –253 J/mol$\cdot$deg and the kinetic dependencies $a_{chlZn}=f\,(T,\tau)$. Based on the results obtained and the latest representations about ZnO defect types, the chemism of ZnO and Cl^- interaction was proposed: fixing of Cl^- on the acceptor centers of ZnO and formation of atomic chlorine ($F+2Cl^-=2Cl^0$); chemisorption of Cl^0 on the donor centers ($V^0_0+2Cl^0+e=2Cl^-_{ads}+2V^0_0$); diffusion of Cl^-_{ads} along the oxygen vacancies of the surface layer and interaction with ZnO ($Zn^x_{Zn}+O^k_0+2Cl^-=ZnCl_2+O+2e$). The intensification of zinc sublimation from $ZnCO_3$ in the presence of O_2 and SiO_2 is associated with the accelerated $CaCl_2$ decomposition and formation of calcium silicates that promote to the shift of the reaction equilibrium to the right.

The industrial testing of the technology was realized together with industrial association "Kazsvinets" at a pilot shop with the capacity of 20 ths Mg of ore per year (Fig. 7).



Additives to the oxides: 1 – Cu_2O+ZnO, 2 – $Cu_2O+Fe_2O_3$, 3 – $Cu_2O+Fe_2O_3$+ZnO, 4 – ZnO+Fe_2O_3, 5 – PbO+Fe_2O_3, 6 – PbO+ZnO, 7 – ZnO+PbO+Fe_2O_3, 8 – PbO+$Cu_2O+Fe_2O_3$,9 – PbO+Cu_2O

Fig. 6. Effect of oxide additives on the Cu, Zn, Pb chloridosublimation degree

Fig. 7. The pilot shop on the processing of oxidized zinc ores

During the testing, the paste-like charge consisting of the crushed ore, ash of a thermal power station, clay and a $CaCl_2$ solution after its preliminary forming and drying was fired in a rotating furnace at 1150-1200 ^{0}C for 45-50 minutes. During the testing period, α_{chl}Zn and α_{chl}Pb were 96.6% and 98.0%. 98-99% of Al, Ca, Fe, Mg, Mn, Ti, Na, K pass into expanded clay. The cinder with the bulk density of 580-990 kg/m^3 can be used to produce construction concrete (grades up to 500) and construction heat-insulation claydite-concrete (M50-M75 grades). The resulting vapor-gas mixture was fed to a gas-purifying system including a cyclone, an adsorber irrigated with a calcium hydroxide solution and a cascade foam apparatus (Institute "Titan" (Zaporozhye). The hydrate cake, obtained of the charge based on the Zhayrem ore, contained after the drying34.0% of Zn, and after the calcining 62-69% of ZnO. The total extraction of Zn into the calcined cake, taking into account the recycled products, was 91.7%, Pb – 94.9%. The $CaCl_2$ regeneration degree was 91.5%. Based on the results obtained, the technological regulations were developed for the transfer of the Zhayrem mining and processing plant to the operation according to the chloride technology with the annual capacity of 130 ths Mg of ore.

3.3. Processing of oxide calcium-containing carbonate zinc-containing ores to produce zinc sublimates, a ferroalloy and calcium carbide

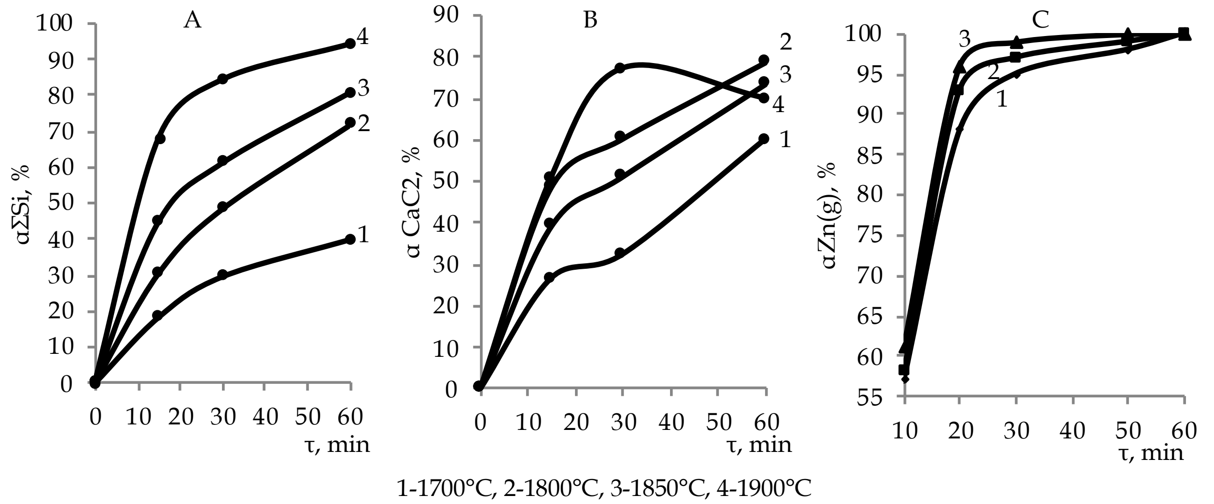
The major part of the information given in this section has been published in (Shevko et al.,2018a; Shevko et al.,2015a; Shevko et al.,2015b; Shevko et al.,2018b; Shevko et al.,2018c; Shevko et al.,2018d; Shevko et al.,2018e; Shevko et al.,2018f; Shevko et al.,2018g; Shevko et al.,2017; Shevko et al.,2014). Some zinc oxide ores contain a significant amount of calcium carbonate. Based on the principle of a universal technological raw material, we have developed a technology for extracting zinc into sublimates, calcium into calcium carbide, and silicon into ferroalloys from the Achisay and Shaymerden ores. The Shaymerden ore consists of 27-33% of calcite ($CaCO_3$), 25-29% of nontronite ($Na_{0,33} \cdot Fe_2 + 3(Si, Al)_4O_{10}(OH)_2 \cdot xH_2O$), 6-10% of hemimorphite [$Zn_4Si_2O_7(OH)_2(H_2O)$], 5-10% of willeminite [$Zn_2(SiO_4)$], up to 10% of lizardite [$Mg_3(Si_2O_5(OH)_4)$], up to 8% of hardistonite ($Ca_2ZnSi_2O_7$), 4-11% of goethite (FeOOH). The content of Zn in the ore is 17-22%, Pb - 0.5-0.6%, Fe - 2.2-2.5%, Si - 9-11%, Ca - 11-18%, Al - 4-6%, Mg - 0.2-0.4%, Mn - 0.2 -0.5%, K - 0.1-0.2%, Ti - 0.1-0.3%, C - 5-8%, Ba - up to 0.1%, S - up to 0.3%, the rest is oxygen. The main non-ore elements in the ore are calcium and silicon (∑Si and Ca = 20-29%). The main minerals of the Achisay ore are: smithsonite ($ZnCO_3$), calamine ($Zn_4(OH)_2 \cdot Si_2O_7 \cdot H_2O$), siderite ($FeCO_3$), calcite ($CaCO_3$), magnesite ($MgCO_3$). The ore contains 9-13% of Zn, 0.3-11% of Pb, 0.1-0.2% of Cd, 14-16% of Fe, 16-24% of CaO, 3-7% of MgO, 3-7% of Al_2O_3, 4-7% of SiO_2, up to 0.3% of S, others (including CO_2 and H_2O) - 15-25%. The main non-ore elements are Ca and Fe ((∑Si and Fe = 25-33%).

The method is based on the reaction:

$$ZnO+CaO+4SiO_2+Fe_2O_3+15C=Zn_g+2FeSi_2+CaC_2+13CO; \quad (13)$$

$$ZnO+CaO+2SiO_2+Fe_2O_3+11C=Zn_g+2FeSi+CaC_2+9CO. \quad (14)$$

From the thermodynamic point of view, these reactions are possible at $T \geq 1341^0C$andT$\geq 1183^0C$, respectively. The kinetics of Zn distillation from the Shaymerden ore (20.84% of Zn, 0.86% of Pb, 2.53%of Fe, 0.14% of Cd, 21.04% of SiO_2, 15.68% of CaO, 7.21% of Al_2O_3) and the transition degree of Si in an alloy and Cain calcium carbide were investigated (Fig. 8).



1-1700°C, 2-1800°C, 3-1850°C, 4-1900°C

Fig. 8. Temperature and time influence on the silicon transition degree in a ferroalloy (A), calcium in calcium carbide (B), and zinc in sublimates (C) from the Shaymerden ore

The kinetics of the Zn sublimation, Si transition in alloy and Ca transition in calcium carbide obeys the equation $\alpha=1-\exp[-k \cdot \tau^n]$. The extraction of silicon in alloy and calcium in calcium carbide is restrained by kinetic factors. The activation energy of the processes is 344-499 and 405-524 kJ, respectively. The zinc sublimation is restrained by diffuse phenomena and is characterized by the activation energy of 11.7 kJ.

The data obtained during the electric melting in an arc furnace allowed us to establish the regression equations for change in the extraction degrees of Si in the alloy (α_{Si}, %) and Ca in CaC_2 (α_{CaC2}, %), Si concentration in the alloy (C_{Si}, %) and the calcium carbide capacity (L, dm^3/kg):

$$\alpha_{Si} = 90.978+0.1287 \cdot St-2.226 \cdot K+0.002 \cdot St^2+0.0477 \cdot K^2-0.0126 \cdot St \cdot K; \quad (15)$$

$$C_{Si} = 80.404-1.42 \cdot St-1.726 \cdot K+0.0154 \cdot St^2+0.0315 \cdot K^2-0.005 \cdot St \cdot K; \quad (16)$$

$$\alpha_{CaC2} = 173.873-0.95 \cdot St-8.359 \cdot K-2.029 \cdot 10^{-2} \cdot St^2+0.149 \cdot K^2+3.78 \cdot 10^{-2} \cdot St \cdot K; \quad (17)$$

$$L = 1617.65-0.4623 \cdot St-92.198 \cdot K-0.048 \cdot St^2+1.498 \cdot K^2-0.1235 \cdot St \cdot K. \quad (18)$$

These equations were a basis for construction of volumetric and planar (Fig. 9) images of the coke (K, %) and steel shavings (St, %) effect on the response parameters. As follows from the figure, the silicon content in the alloy varies from 19.6 to 42%, and the silicon extraction in the alloy is 66.2-77.0%. According to the silicon content, the resulting alloy corresponds to requirements of the interstate standard (Shevko and Aitkulov, 2012) and belongs to three grades of ferrosilicon: FS20 (Si from 19 to 23%), FS25 (Si from 23 to 29%), FS45 (Si from 41 to 47%). The capacity of the calcium carbide changes from 110 to 250 dm^3/kg. The high capacity calcium carbide (210-250 dm^3/kg) is formed at the great amount of coke (38-40%) (the iron amount is 16-29%). In this case, the extraction degree of calcium into calcium carbide is 77-81% (Fig. 9). The process of reducing and extracting zinc into the gas phase does not limit the technology. So, in all the cases, the Zn extraction degree in the sublimates was not less than 99.3-99.8%.

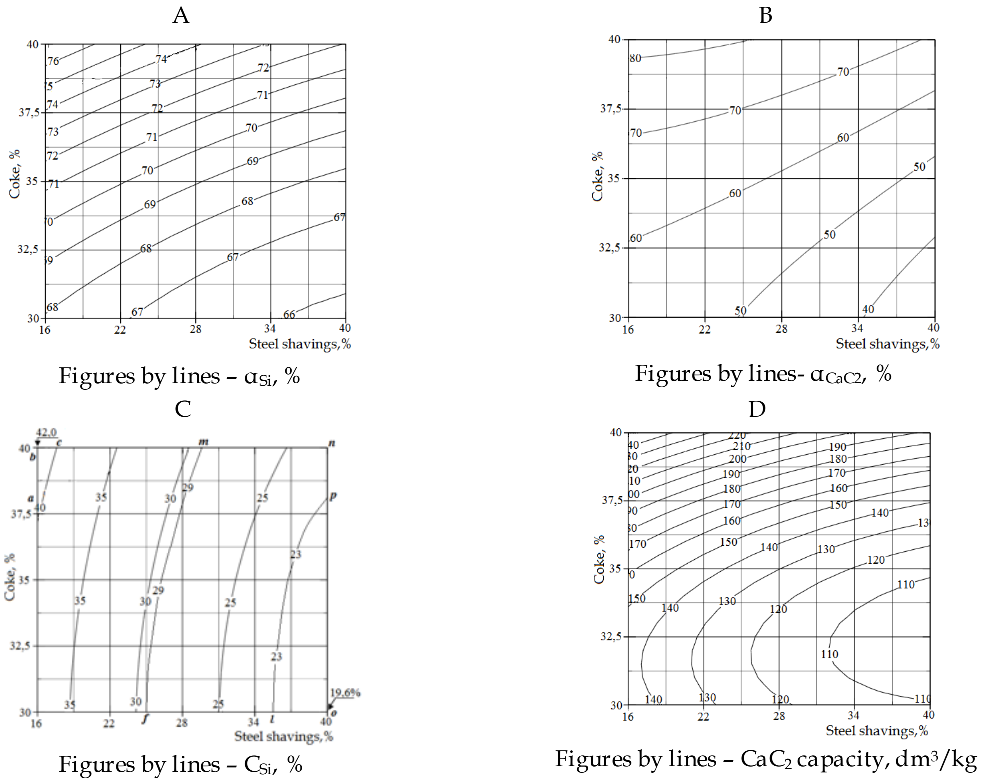
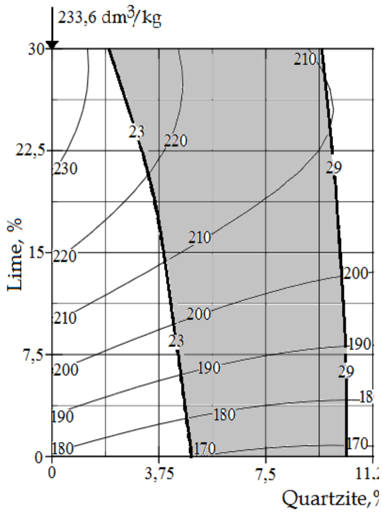


Fig. 9. Influence of coke and steel shavings amounts on the extraction degree of silicon in the alloy (A), the transition degree of calcium to calcium carbide (B), the silicon content in the alloy (C) and the calcium carbide capacity (D) during the electric smelting of the Shaymerden ore

Fig. 10 shows the combined information about the technological parameters of Achisay ore electric smelting (10.1% of Zn, 12% of Ca, 17.1% of Fe, 0.4% of Pb, 2.7% of Si, 1.1% of Na, 3.8% of Mg, 11.8% of C, 40.7% of O). The ferrosilicon obtained contains no more than 29.8% of silicon. When obtaining the FS25-grade ferrosilicon (shaded area of the Fig. 11), calcium carbide had the capacity of 169-227 dm^3/kg, and when obtaining the FS20-grade ferrosilicon, the calcium carbide capacity was 171-233.6 dm^3/kg. The silicon extraction level was from 77 to 79.5%, and the calcium one – 74-80%. The extraction of Zn and Pb in the sublimates is not less than 99,4-99,5%. According to the chemical analysis the sublimates contain 53-57% of ZnO and 1.9-2.2% of PbO.



(-) silicon content in the alloy, %

(-) calcium carbide capacity, dm^3/kg

Fig. 10. Combined information about the effect of lime and quartzite amounts on the Si content in the ferroalloy and the calcium carbide capacity during the electric smelting of the Achisay ore

The results obtained when conducting the large-scale laboratory tests in an electric furnace with power of 45 kW·A showed that the products of smelting the Achisay (Shaymerden) ore are a ferroalloy containing 13-38 (19-46) % ofΣ(Si+Al), calcium carbide with capacity of 161-352 (160-351) dm^3/kg and sublimates containing 44-46 (66-70) % of Zn. The extraction degrees of silicon in the alloy, calcium in calcium carbide and zinc in sublimates were 84-89%, 78-83%, 99.1-99.8%, respectively. Photos of the calcium carbide, alloy and sublimates obtained from the ore are shown in Figs. 11-16.

The sublimates contain 66,42% of Zn (Fig. 16); this value is more than the Zn content in the industrial sublimates produced by the Waelz process by 12-16% (Romanteyev et al., 2006).

During the electro smelting of the ores to obtain calcium carbide and a ferroalloy, up to 40-60% of Mg, Na, and K pass into sublimates, and 80-85% of Ti, V, Cr, Mn pass into an alloy.

For five basic elements (Zn, Pb, Si, Ca, Fe), the coefficient of complex use of raw materials (γ) for the suggested method of processing the Shaymerden zinc oxide ore is:

A B

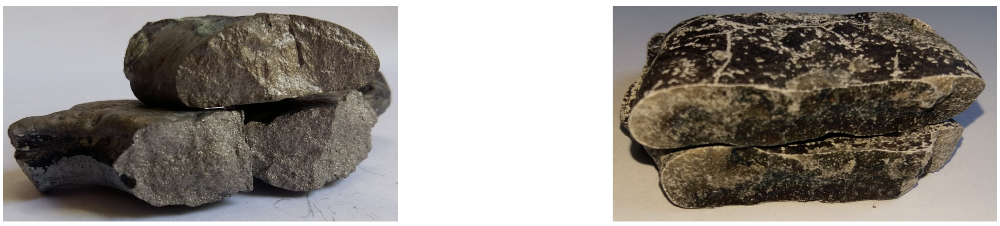
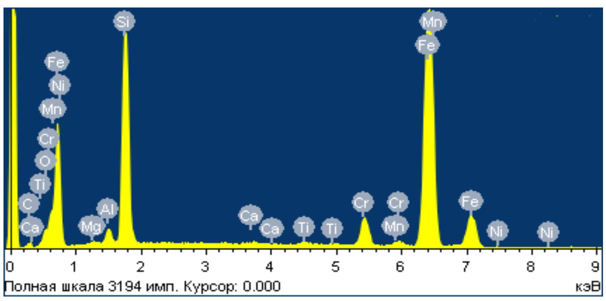
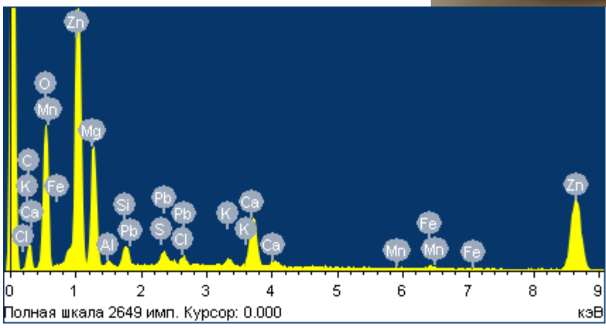


Fig. 11. Ferroalloy (A) and calcium carbide (B) produced from the Achisay ore



Element	Content, %	Element	Content, %
Mg	0,11	Cr	14,75
Al	1,57	Mn	0,25
Si	20,52	Fe	61,6
Ca	0,45	Ni	0,3
Ti	0,45		

Fig. 12. Scanning electron microscopy of the ferroalloys (Achisay ore)

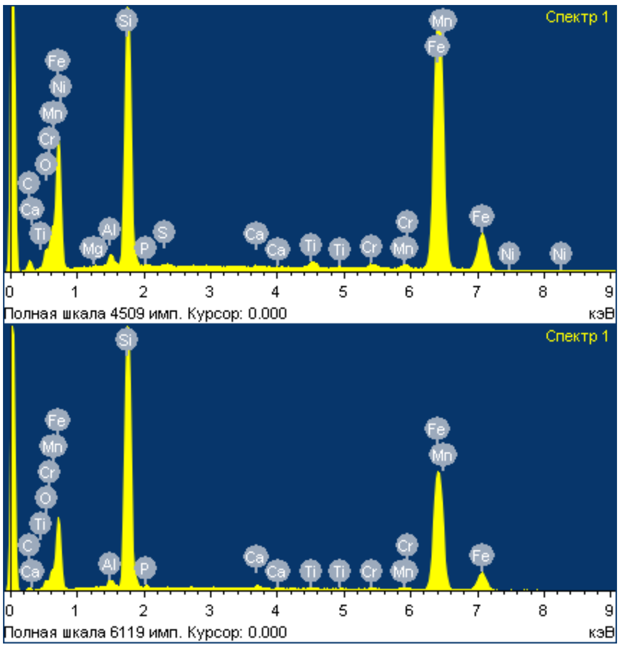


Element	Content, %	Element	Content, %
O	29,33	K	0,63
Mg	14,78	Ca	4,66
Al	0,61	Mn	0,16
Si	1,72	Fe	0,63
S	0,68	Zn	44,34
Cl	0,69	Pb	1,76

Fig. 13. The sublimates (Achisay ore)

A B C

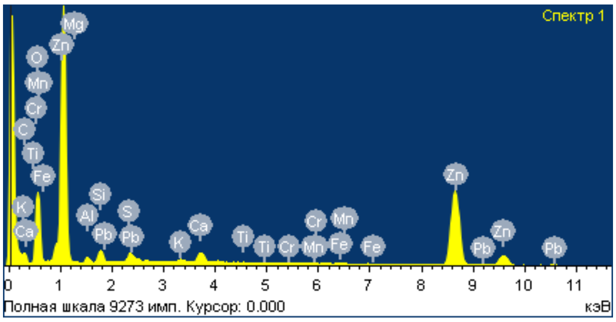
Fig. 14. Ferroalloy (A, B) and calcium carbide (C) (Shaymerden ore)



Element	Content, %	Element	Content, %
Al	1,13	Ti	0,51
Si	29,83	Cr	0,67
P	0,43	Mn	0,79
Ca	0,20	Fe	66,43

Element	Content, %	Element	Content, %
Al	1,22	Ti	0,20
Si	39,54	Cr	0,16
Ni	0,26	Mn	0,49
Ca	0,39	Fe	57,75

Fig. 15. Scanning electron microscopy of the ferroalloys (Shaymerden ore)



Element	Content,%	Element	Content, %
C	6,46	K	0,34
O	19,1	Ca	1,36
Mg	0,44	Ti	0,07
Al	1,02	Cr	0,00
Si	1,68	Mn	0,32
S	0,69	Fe	0,47
Pb	1,65	Zn	66,42

Fig. 16. Scanning electron microscopy of the sublimates (Shaymerden ore)

$$γ=(99.6(Zn_{subl})+99.2(Pb_{subl})+89(αSi_{alloy})+88.3(αCa_{CaC2})+82.8(αFe_{alloy}))/5=91.78\% \quad (19)$$

The same coefficient for the Waelz process is equal to:

$$γ=(88(Zn_{subl})+92(Pb_{subl})+0(αSi)+0(αCa)+0(αFe))/5=36.0\% \quad (20)$$

Thus, the coefficient of complex use of raw materials for the developed technology, in comparison with the existing one, is greater by 91.78/36.0=2.54 times.

3.4. Processing of oxidized copper-containing ores by the chloride reduction-sublimation method

The material of this section has been published in (Shevko et al.,2014a; Shevko et al.,2014b; Aitkulov et al.,2009; Aitkulov et al.,2010; Shevko et al.,2011; Shevko et al.,2009; Shevko et al.,2018h). A characteristic feature of Kazakhstan oxide and mixed copper ores is a high content of silicon oxide. Copper in the ores (0.3-3.7%) is as chrysocolla $[(Cu,Al)_2H_2Si_2O_5(OH)_4 \cdot nH_2O]$ and dioptase $[Cu_6(Si_6O_{18})\cdot 6H_2O$ $(CuOSiO_2\cdot H_2O)]$. The ores contain 50-78% of SiO_2, 8-22% of Al_2O_3, 2-5% of CaO, 0.5-1.8% of MgO, 5-15% of iron oxides, 0.2-1.5% of FeS_2, and also <0.002% of Co, <0.002% of Sb, <0.03% of As, <0.002% of Mo, <0.1 g/t of Au, <13 g/t of Ag.

High SiO_2 and low CaO contents predetermine obtaining a siliceous ferroalloy from such the ore. However, the complete transition of copper to a ferroalloy greatly restricts its sales. Therefore, the copper must preliminary be extracted, for example, by chloride sublimation, and then the resulting cinder can be applied to produce a ferroalloy.

Using a thermodynamic prediction method, it was found that the copper chloride sublimation, regardless of the ore type, is accompanied by formation of several chlorides: CuCl, Cu_2Cl_2, Cu_3Cl_3, Cu_4Cl_4. The typical effect of temperature on the equilibrium copper distribution degree on the example of the Aktogay ore chlorination (0.42% of CuO, 0.08% of CuS, 68% of SiO_2, 5% of Fe_2O_3, 1% of FeS_2, 15% of Al_2O_3) is represented in Fig. 17. The total transition of copper into gaseous chlorides is completed at

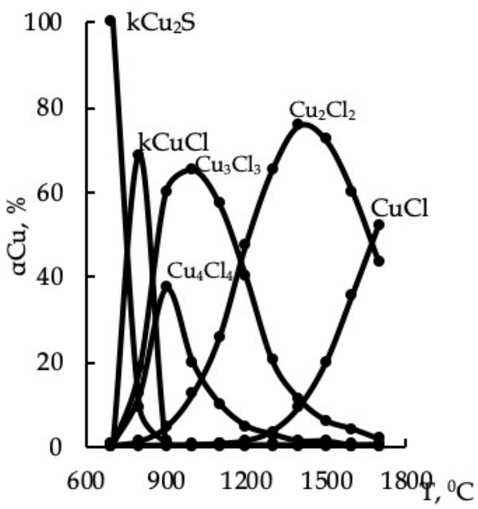


Fig. 17. Temperature effect on the copper distribution degree from the Aktogay ore

0.1 MPa and 900 ^{0}C. In accordance with the Le Chatelier rule, reducing the pressure to 0.001 MPa decreases the temperature of the total copper transition in gaseous chlorides to 700 ^{0}C. The maximum temperature of total transition of copper in the chlorides depends on the type of ore.

For example, for the ore of the Bozshakol deposit (0.6% of CuO, 0.1% of CuS), it is 1500^{0}C. It is important that the degree of iron chloride sublimation in the presence of water at 1100-1200 ^{0}C does not exceed 0.1%.

The kinetics of copper chloride sublimation was studied in the temperature range of 1173-1473 K for ores of the following deposits: Aktogay (0.42% of CuO, 0.08% of CuS), Sayak (0.7% of CuO, 0.5% of CuS), Kalmakyr (0.49% of CuO, 0.21% of CuS), and Maldybay (0.61% of CuO, 0.23% of CuS). The research results are shown in Table 3.

Table 3. Kinetics of copper chloride sublimation at 1373 K

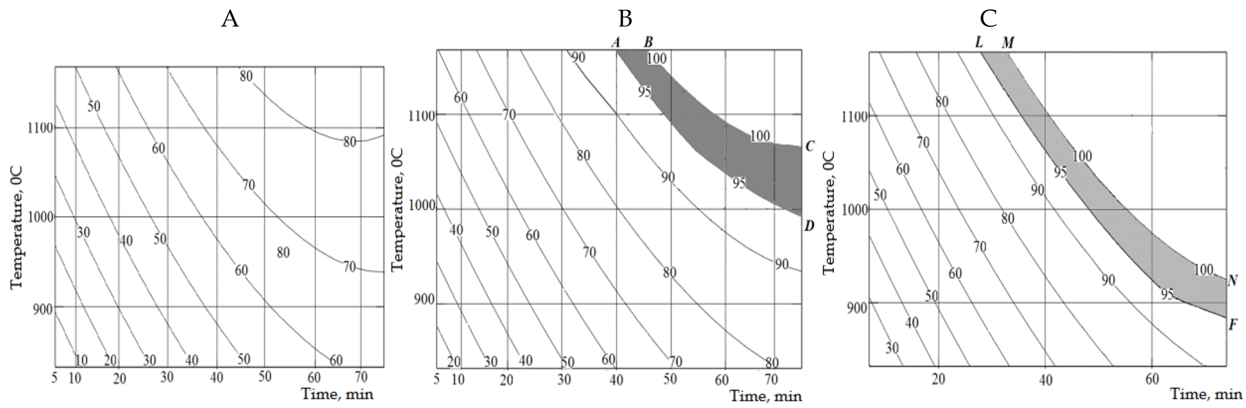
Ore	Time, min				Activation energy,kJ	Activation energy of the beginning of the reaction, kJ
	5	20	30	45		
Aktogay	50,1	80,0	90,3	96,9	45-48	70,6
Sayak	58,1	76,0	88,4	98,4	49-58	79,9
Kalmakyr	60,4	79,2	93,6	99,6	48-62	118,3
Maldybay	51,6	70,0	81,6	94,9	50-86	164,6

Judging by the data, the chloride sublimation of copper almost completely ends in 45 minutes and it occurs in the diffusion (Aktogay, Sayak) or mixed (Kalmakyr, Maldybay) regimes. Moreover, the period of the process initiation is characterized by the activation energy from 70.6 (Aktogay) to 164.6 kJ (Maldybay). It should be noted that 85-90% of gold and silver pass into sublimates.

The research carried out by the method of experimental planning allowed us to determine the regression equation of influence of the temperature, time and $CaCl_2$ amount on the copper chloride sublimation degree from copper oxide ores. For example, for the Sayak ore, the equation has the form:

$$\alpha_{chlCu}=-200.61+2.39\,\tau+0.21\cdot T+7.32\cdot CaCl_2-1.2\cdot10^{-3}\,\tau^2-4.9\cdot10^{-5}\cdot T^2-0.41CaCl_2^{\,2}-9.2\cdot10^{-4}\,\tau\cdot T+ +0.043\,\tau\cdot CaCl_2+3.8\cdot10\text{-}3\cdot T\cdot CaCl_2 \quad (21)$$

Using this equation we constructed the planar pictures of α_{chlCu}=f(τ, T) for constant $CaCl_2$ (Fig.18).



A – 6%of $CaCl_2$, B – 8% of $CaCl_2$, C– 10% of $CaCl_2$

Fig. 18. Temperature and time effect on the copper sublimation degree (Sayak ore)

Fig. 18 shows that at 6% of $CaCl_2$, the α_{chlCu} does not reach 90 %, and at 8% of $CaCl_2$, the high α_{chlCu} (from 95 to 100 %) can be reached in the conditions of the ABCD area. At 10 % of $CaCl_2$, the α_{chlCu} higher than 95 % can be achieved at the lower temperature and duration (LMNF area). The complete chloride sublimation of copper occurs at 1100^{o}C in 42 minutes or at 1000^{o}C in 56 minutes. Similar pictures were constructed for other ores (Maldybay, Zhezkazgan, Kalmakyr, Aktogay, Bozshakol).

The enlarged-laboratory tests of the chloride roasting of granulated ores with catching the copper chloride sublimates were carried out in a rotating furnace RF 2.13/14, manufactured by "Uralelectropech" LLC. The furnace capacity is up to 35 kg of charge per hour. The dry catching was fulfilled in a system including coolers and a bag filter, and the wet one – in a system consisting of coolers, a scrubber irrigated with a sodium chloride solution, a drop catcher and a solution receiver.

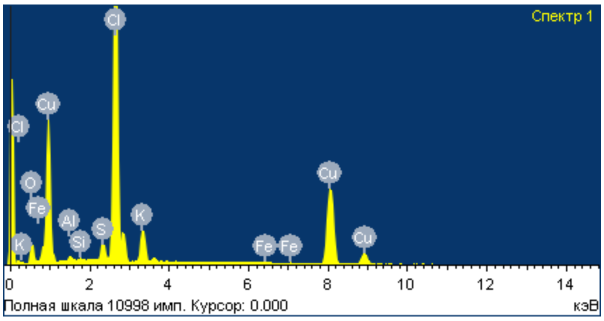
The technological parameters of the process in a case of the dry catching of sublimates are shown in Table 4.

The chloride sublimation roasting allows us to extract 92-98% of copper in the sublimates (the catching degree – 94.6%). The sublimates contain 28-51% of copper (Fig. 19). The copper content in the sublimates is significantly higher than one in copper concentrates (13-36%).

Copper from the dry sublimates was produced by cementation with iron. Samples of the resulting copper are represented in Fig. 20.

Table 4. Technological parameters of chloride sublimation roasting of copper-containing ores with dry catching of sublimates

Ore	Cu content in ore, %	Roasting temperature, ^{0}C	Cu sublimation degree, %	Duration of staying the charge in the roasting zone, min	Cu content in sublimates, %
Sayak	1,0	1013-1040	96-97	53-62	36-37
Shatyrkol	3,7	1000-1030	94-96	50-54	39-42
Bozshakol	0,54	1000-1040	96-98	56-64	30-32
Karagaily	0,36	980 -1020	92-93	60-66	28-33
Zhezkazgan	1,45	1010-1030	94-96	58-63	31-34
Nurkazgan	0,98	970 -1000	92-94	61-63	35-36
Aktogay	0,5	990 -1020	95-97	57-62	33-36
Moldybay	0,64	1030-1080	92-95	54-57	36-38



Element	Content,%	Element	Content, %
Cl	34.59	S	1.43
O	7,65	K	4.63
Al	0,51	Fe	0.24
Si	0,13	Cu	50.81

Fig. 19. Scanning electron microscopy of the sublimates (Sayak ore)

A B C

A–washed coppe; B– dried copper; C –fused copper

Fig. 20. Copper samples

The fused copper contained 72.5-82.6% of Cu. The copper extraction degree from the solution was 97.2-98%. The wet system provided catching of99.6% of copper chloride. The metal from the "wet" solutions containing 10.6-11.1 g/l of copper was extracted by cementation at 60-65^{0}C during 2-15 minutes at pH=4.5. The dried and fused copper contained 68-79.8% of the metal. During the roasting, 98-99% of aluminum, calcium, magnesium, manganese, iron, sodium and potassium oxides pass into the cinder.

The cinders obtained as a result of the reduction-chlorinating roasting of the copper ores containing 60-77% of SiO_2 and less than 0.1-0.15% of Cu were used for smelting ferroalloys.

Previously, the influence of temperature and carbon and iron amounts on the transition degree of silicon in ferroalloy was determined by thermodynamic modeling. For example, for the Sayak cinder, it was found that the maximum transition of silicon in the alloy can be reached when the process temperature is 1700-1800^{0}C, the carbon amount is 120-140% of the quantity theoretically necessary for the silicon and iron reduction, and the iron amount is equal to 100-120% of the quantity theoretically necessary for formation of the alloy containing 55% of Fe and 45% of Si.

The study of the kinetics of obtaining ferroalloys from the cinders of chloride sublimation roasting showed that the silicon transition degree into the alloy at 1700 ^{0}C for 45-60 minutes is 73-81%. The relationship was found between the activation energy (*E*) of the reaction generation period and the cinder's chemical composition (and namely, its acidity modulus: $AM=\Sigma SiO_2+Al_2O_3/\Sigma CaO+MgO$); $E=490{,}69-19{,}093AM+0{,}5003AM^2$. That is, the reduction of silicon from the cinder with a high SiO_2 concentration occurs more intensively than its reduction from the cinder with high basicity.

Using the results obtained during the electric melting of the cinder (Sayak ore) the regression equation was determined explaining the coke and steel shavings amounts effect on the silicon concentration in the alloy; this equation was applied for construction of a planar picture of $C_{Si}=f(C, St)$ (Fig. 21).

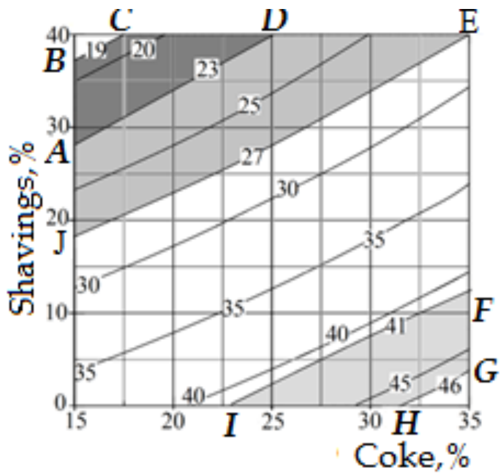


Fig. 21. Influence of the coke and steel amounts on the silicon content in the alloy

The figure shows that ferrosilicon of FS20, FS25 and FS45 grade scan be produced in the planes of ABCD (coke from 15 to 25%, shavings from 28 to 40%), ADEJ (coke from 15 to 35%, shavings from 18 to 40 %) and IFGH (coke from 23 to 35%, shavings from 0 to 12 %). During the production tests, 145 Mg of the charge was processed. The tests were conducted at the pilot plant of RPC "Kazhiminvest". The cinder formed from the Sayak ore contained 54.2% of SiO_2, 12.8% of Fe_2O_3, 18.9% of CaO, and 8.8% of Al_2O_3. The tests showed that the major part of silicon (66-72%) passes into the ferroalloy, which contains 41.8% of Si. The electric power consumption is 4700-4900 kWh per 1 Mg of the ferroalloy. The furnace operated according to the mixed mode (based on current and voltage oscillograms). The hydrometallurgical processing of dry sublimates and chloride solutions provides for production of cement copper, zinc oxide and iron concentrates. Zinc oxide concentrate is processed according to the classical scheme to produce cathodic zinc, and iron concentrate is used inside the scheme to produce ferroalloys.

The raw materials complex uses coefficient (γ) for the suggested technology of processing the copper oxide ores for three elements (Cu, Si, Fe) taking into account levels of copper chloride sublimation, copper extraction from the sublimates into solution and copper extraction from the solution into crude copper by cementation – 91%, 96% and97.6%, respectively – is:

$$\gamma=([91{,}0(\alpha Cu_{subl})*96.0(\alpha Cu_{sol})*97.6(\alpha Cu_{crude})]+68.6(\alpha Si_{alloy})+86.3(\alpha Fe_{alloy}))/3=83.6\% \quad (22)$$

The degree of copper extraction in cathode copper during the hydrometallurgical processing of the copper ore using the SX-EW method is 87.6%, and silicon and iron after the leaching remain in dumps. Then:

$$\gamma_{hydromet}=(87.6(Cu_{cath})+0(\alpha Si)+0(\alpha Fe))/3=29.2\% \quad (23)$$

So, the γ for the method developed by us, in comparison with the existing way, is greater in 83.6/29.2=2.86 times.

The principle of a universal technological raw material can be used for processing other natural and man-made raw materials. So on the basis of basalts of deposits Daubaba and Dubersay, we have developed technologies for production of ferroalloys and calcium carbide (Aitkulov et al., 2007; Shevko et al.,2019c). When the electric melting the Achisay waste clinker we obtained the FS20 and FS25-grade ferrosilicon and zinc oxide sublimates, at that the zinc and lead extraction degrees into the sublimates were nearly 100% (Shevko et al., 2009c). We also used this principle for processing the overburden rocks by the chloride sublimation method. The given technology passed industrial testing. It allowed us to extract non-ferrous metals into chloride concentrate and simultaneously produce agloporit from the non-metallic component (Shevko and Daribayev, 2004).

4. Conclusions

Modern production of non-ferrous metals is imperfect due to the loss of rock mass and metals in the process chain from mining to metal production. Processing of zinc and copper ores by hydrometallurgical and pyrometallurgical methods involves formation of dump cakes, clinkers, and flotation – formation of tailings. For this reason, they are characterized by a low coefficient of complex use of raw materials (for example, for the Waelz process no more than 35%). To increase a level of complex processing of oxide raw materials, it is necessary to change the attitude to raw materials and create a technology based on new principles.

Theoretical regularities, features and optimal technological parameters of new methods of complex processing of oxide, oxidized and mixed zinc ores were determined, based on the ideology of a universal technological raw material and the principle of simultaneous production of several products in one furnace unit.

The following new technologies have been developed:

- electric smelting of oxidized silicon-containing zinc ores of the Shalkiya and Zhayrem deposits to produce ferrosilicon of FS20, FS25 and FS45 grades and zinc sublimates containing 51-53% of Zn;
- chloride sublimation roasting of the Zhayrem oxidized ore to obtain the concentrate containing 62-69% of ZnO and expanded clay for construction concrete;
- electric melting of oxide carbonate ores of the Shaymerden and Achisay deposits to produce calcium carbide with capacity of 160-350dm^3/kg, the ferroalloy containing 19-46% of ΣSi and Al and zinc sublimates with Zn concentration of 41-70%;
- chloride sublimation roasting of oxidized mixed ores of the Sayak, Aktogay, Shatyrkol, Nurkazgan, Moldybay, Zhezkazgan and Karagaily deposits to produce chloride sublimates (28-51% of Cu) and silicon-containing cinder; processing of the sublimates by cementation allowed us to extract 97-98% of copper into the crude metal containing 72-82% of Cu, and the cinder is applied for obtaining ferrosilicon of FS20, FS25b and FS45 grades.

The developed technologies allow to significantly increase the raw materials’ complex use degree, for example, in the case of processing zinc oxide ores and production of ferroalloy, calcium carbide and zinc sublimates (in comparison with the Waelz process) – from 36.0 to 91.8%, and when processing copper oxide ores to obtain crude (cement) copper and ferroalloy (in comparison with the SX-EW process) from 29.0 to 83%.

The principle of a universal technological raw material can be used for processing other natural and man-made raw materials. So, using the developed technologies the Daubaba and Dubersay basalts can be processed into ferroalloys and calcium carbide. Processing the Achisay waste clinkerby electric melting according to the suggested technology gives the possibility to produce the FS20 and FS25 grade ferrosilicon and completely extract zinc and lead into zinc oxide sublimates. The same principle was used by us at the chloride sublimation of overburden rocks. The method, which has passed industrial testing, allowed us to extract non-ferrous metals into chloride concentrate and simultaneously obtain agloporit from the non-metallic component.

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