Thermodynamic and Experimental Substantiation of Comprehensive Processing of Zinc Sulfide Ore and Its Concentration Tailings to Extract Non-Ferrous Metals and Produce a Silicon Ferroalloy

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Abstract: This article presents the results of thermodynamic and experimental studies on the joint processing of a mixture of Shalkiya deposit zinc-lead sulfide ore and its concentration tailings in the presence of coke and magnetite. Using the HSC-6.0 software package, it was established by thermodynamic modeling that the silicon-containing products of the SiO2 reduction in the system under consideration are FeSi, Si, Fe3Si, Fe5Si3, FeSi2, FeSi2.33, and SiOg, which, based on the starting reduction temperature, form an increasing series: Fe3Si (1200 °C); Fe5Si3, Si (1400 °C); and SiOg, FeSi2, FeSi2.33 (1500 °C). The smelting of the zinc-lead sulfide ore and concentration tailings mixture in the case of replacing 55% of the iron contained in the magnetite concentrate with steel shavings iron allowed us to produce FeSi45 ferrosilicon (41.9%–42.1% Si), with the extraction of 85% of the silicon in it, and sublimates containing 26.03% zinc and 13.47% lead, with the extraction of 97% of the zinc and 99% of the lead in them. In comparison with the initial ore-tailings mixture, the resulting sublimates are 11.83 times richer in zinc.

Keywords: zinc-lead sulfide ore; concentration tailings; magnetite; carbon-thermal reduction; thermodynamic model; electric smelting; ferroalloy; lead-zinc sublimates

1. Introduction

According to the US Geological Survey, at the beginning of the 21st century, the world zinc reserves amounted to 190 million tons, and also taking into account the proven zinc reserves in Kazakhstan (34.5 million tons), no less than 230 million tons [1,2]. Most (75%–80%) of the world’s zinc is produced from sulfide ores [3] according to the following scheme: ore → grinding → concentration → roasting → leaching → solution purification → electrolysis → zinc cathode. This method is constantly being improved. Thus, new methods for the concentration of zinc sulfide ores are described in [3–27]. For example, according to [4], to selectively increase the flotation activity of sulfides, different ratios of sulfhydryl collectors are used. To improve zinc extraction during collective flotation of a sulfide ore, it is proposed to use machine oil. The method makes it possible to increase the extraction level of zinc from the ore by 6.25%–9.1% [5]. To increase the depression degree of sulfide minerals, it is recommended to use a mixture consisting of Na2S, Na2SO3, and ZnSO4 in the ratio of $\Sigma Na_2S + Na_2SO_3 / ZnSO_4 = 1.2$ [6]. To increase the separation intensity when concentrating sulfide materials, it is proposed to use different ratios of Na2S, ZnSO4, and Na4S2O5 equal to (0.5:1.5):1:(3:0.5) [7]. The work [8] describes the results of studies on the processing of refractory zinc and lead ores. The method consists of combining open
direct selective flotation with the addition of a pyrite depressant reagent during the carrying out of cleaning operations to produce zinc concentrate and hydrometallurgical processing of the lead–zinc intermediate product. The total extraction degree of the zinc into the concentrate (53% of Zn) and the productive solution is 74.6%. To improve the technological parameters of lead–zinc ore flotation, work [9] presents results on the use of a consortium of Ochrobactrum anthropic and Psychomonas aeruginosa JCM 5962 microorganisms in the concentration process. It is shown that in this case, the extraction degree of the metals into the collective concentrate increases by almost 40%. For the effective selection of flotation reagents for sulfide ores, patent [10] proposes to use a computer program that takes into account not only the metal content in the ores but also the dipole/dipole interaction of the reagents, Van der Waals interaction, bond angle bending, stretching of valence bonds, and steric energy. Preliminary gravitational concentration (enrichment in heavy suspensions) of zinc–lead ores containing 0.75% lead, 3.47% zinc, 49.63% silicon dioxide, 10.81% copper oxide, and 5.99% carbon showed that the yield of the light fraction of concentration tailings was 18.8% of the ore and contained 1.9% of the zinc, 0.42% of the lead, and 69.50% of the silicon dioxide, and the content of zinc and lead in the heavy fraction increased three to four times [11]. Additional information on the beneficiation of Zn–Pb ores can also be found in [12–14]. Speaking about roasting sulfide concentrates, it is necessary to focus on several works. Thus, in [15], to increase the productivity of the fluidized bed furnaces used for roasting zinc concentrates, it is proposed to add wastewater treatment sludge (62%–68% Ca(OH)₂) and 17%–30% Zn into the charge. This technique significantly reduces the coarsening of particles and sticking of the material on the hearth. Due to this, the furnace productivity increases by 1.3 times. For roasting low-grade zinc concentrates with a high content of impurities (16%–24%) without formation of incrustation on the bottom of the fluidized bed furnace and emissions of dust and gas from the furnace, work [16] describes the results of studies on combining the granulation, calcination, hardening, and roasting processes in one unit at a temperature of 1173–1273 K. The developed technology made it possible to increase the furnace productivity by 1.6 times (from 2.4 to 3.9 t/m² per day). To reduce the formation of zinc silicates and zinc ferrites during the roasting of zinc concentrates, the process is carried out in the presence of limestone [17]. This allows for the increase in the degree of zinc extraction into solution by 8.4%.

Along with the traditional method of processing zinc ores, other methods are known and are being developed, for example, autoclave leaching [28–34]. Thus, the results described in works [30,31] show that in two-stage leaching, a concentrate containing <49% Zn at 150–160 °C and 0.3–0.8 MPa allows extracting at least 95% of the zinc into solution. Autoclave leaching concentrates containing 26%–42% Zn using a surfactant (2–3 kg/t of concentrate) at 1.1 MPa allows extracting 98.4%–98.7% of the Zn into solution [32,33], and work [34] contains the results of studies on the extraction of zinc from concentrates in the presence of combined surfactants (ligosulfonate, alkylaryl sulfonate). Conditions have been found that make it possible to increase the extraction degree of zinc into solution by 17.1%. A combined method has been developed for processing a difficult-to-process lead–zinc ore (5.96% Zn, 1.06% Pb) [35], which makes it possible to extract 55.64% of the zinc into concentrate (48% Zn) and another 29.4% into metal. Simultaneously, 51.2% of the lead is extracted into a lead concentrate containing 75% Pb. At the same time, silver goes into commercial products (Dore alloy, Zn concentrate) at 69.2%. Another combined method [36] suggests initially producing a coarse zinc concentrate and a high-quality lead concentrate. Then, >80% of the Zn is extracted from the zinc concentrate into solution by bioleaching. There is also a chlorine-ammonium method for processing a high-siliceous sulfide ore (4.3% Zn and 7.6% Pb), which makes it possible to extract 97% of the Zn into ZnO and 95% of the lead into PbCl₂ [37,38].

Percolation leaching has been used to process a high-siliceous ore (68.7% of SiO₂) containing 1.45% Zn and 5.4% Pb. This is an oxide–sulfide ore with zinc and lead oxidation levels of 56 and 41%, respectively [39]. At the first stage, the ore is leached with sulfuric acid to extract 76.2% of the zinc, and at the second stage with a sodium chloride solution to
extract 69.1% of the lead. To extract metals from the solutions into independent products, iron is separated by a hydrolytic method, zinc is precipitated with sodium carbonate, and lead is precipitated with calcium oxide in the form of hydroxychloride.

Despite a fairly large amount of research in the field of hydrometallurgical processing of zinc sulfide ores, the results of these studies do not completely solve the problems of the processing. The main problems of processing zinc–lead sulfide ores are associated with the insufficiently high extraction degree of zinc into concentrate and the formation of a large-tonnage production waste—concentration tailings [40]. These problems are now having a major impact on the processing of the Shalkiya deposit sulfide ore, the balance reserves of which are 129.35 million tons, and the off-balance reserves of which are 119.56 million tons [41]. When concentrating the Shalkiya ore, containing 3.5% Zn and 0.87% Pb, 0.91 tons of concentration tailings are formed per 1 ton of the ore. During the processing, 19% of the zinc and 43% of the lead are lost with the tailings containing 0.6%–0.9% Zn and 0.6%–0.8% Pb. Ore beneficiation, based on the difference in physical and physicochemical properties of individual grains of minerals, ensures the achievement of satisfactory results only in those cases when crushing and grinding of the rock mass makes it possible to obtain relatively homogeneous grains of minerals that differ in their properties from waste rock minerals [42–44]. Therefore, additional problems arise with the processing and disposal of tailings formed at the concentration of not only zinc ores but also other ores [45–52]. A distinctive feature of the Shalkiya sulfide ore and its concentration tailings is the significant amount of silica in them (at least 50%) [41], so they are of great interest as a raw material not only for non-ferrous metallurgy but also for the production of silicon-containing products, for example, silicon-containing ferroalloys.

The aim of this study was to determine the possibility of the complex processing of the Shalkiya sulfide ore and its concentration tailings to obtain ferroalloy and extract zinc and lead into sublimates.

This article presents the results of studies on the joint processing of the Shalkiya sulfide ore and its concentration tailings with the extraction of zinc and lead and the production of ferroalloy.

2. Materials and Methods

The studies were carried out using computer thermodynamic modeling and electric melting in an arc furnace. The thermodynamic process prediction was carried out using the HSC-6.0 software package [53] developed by the Finnish metallurgical company Outokumpu. For the computer thermodynamic modeling, the HSC-6.0 Equilibrium Compositions module was used. The database of the program contains information about the enthalpy, entropy, and heat capacity of more than 17,000 substances. The HSC Chemistry program intended for equilibrium calculation is based on the principle of minimizing the Gibbs energy of a thermodynamic system. The equilibrium parameters of a thermodynamic system are determined by solving the mathematical problem of finding the extremum using the Lagrange function. The calculations were carried out using Newton’s method of successive approximations. Bearing in mind the constant updating of thermodynamic characteristics in the database of the HSC software package, the work performed with use of this program has a high degree of reliability [54]. The determination of the equilibrium distribution degree of elements in the systems under study was carried out using an algorithm developed at South Kazakhstan University [55]. The studies were carried out in the temperature range from 500 to 2100 °C, with a step of 100 °C, at a pressure of 1 bar. The following parameters were determined: the effect of temperature and amount of Fe$_3$O$_4$ on the equilibrium distribution degree of silicon, zinc and lead; the extraction degrees of silicon into the resulting alloy and zinc and lead into sublimates; and the concentration of silicon in the alloy. The amount of magnetite varied from 38 to 55% of the mixture mass. The amount of carbon was calculated from the condition of complete reduction of SiO$_2$ to Si and Fe$_3$O$_4$ to Fe and was 35% at 38% Fe$_3$O$_4$ and 39% at 55% Fe$_3$O$_4$. 
Electric melting of the charge was carried out in a single-electrode arc furnace (power up to 15 kVA), lined with chromium-magnesite bricks (Figure 1). The bottom electrode is made of a graphite block. A graphite crucible (d = 6 cm, h = 12 cm) is placed on the hearth. The upper part of the furnace is closed with a removable lid with holes for a 3 cm diameter graphite electrode and gas outlet. The crucible was preheated with an arc for 20–25 min. During the preheating, the current was 250–350 A, and the voltage was 30–40 V. After this, the first portion of the charge (200–250 g) was loaded into the crucible and melted for 5–7 min. Then, every 5–6 min, the 200–250 g charge portions were loaded into the crucible. During the melting period, the current was 350–400 A, and the voltage was 25–30 V. Electricity was supplied to the furnace from the TDZhF-1002 transformer. The required power was maintained by a thyristor regulator. After completion of the electric melting process, the furnace was cooled for 6–7 h. The graphite crucible was removed from the furnace and broken. The ferroalloy was weighed and analyzed for metals using an AASnovAA800 atomic absorption spectrometer (Jena, Germany) and a JSM-6490LV scanning electron microscope (Tokyo, Japan) with INCA Energy energy-dispersive micro-analysis and HKL-Base structural analysis systems in the regional testing laboratory of the engineering profile “Structural and Biochemical Materials” (M. Auezov South Kazakhstan University, Shymkent, Kazakhstan) using the method of electron microscopic study of the microstructure and X-ray energy-dispersive microanalysis of materials. To ensure their good electrical contact with the stage and to fix the samples when the stage was tilted, special conductive adhesives were used.

The results of the X-ray phase analysis of the Shalkiya sulfide ore are shown in Figure 2. X-ray diffraction analysis was performed on an automated diffractometer DRON-3 (Russia) with CuKα radiation, β-filter. Conditions for recording diffraction patterns: \( U = 35 \text{kV}; I = 20 \text{mA}; \text{recording} = 0–20 \text{deg/min}; \text{detector} = 2 \text{deg/min}. \) Semi-quantitative X-ray phase analysis was performed on the diffraction patterns of powder samples using the method of equal weighed portions and artificial mixtures. Quantitative ratios of crystalline phases were determined. The diffraction patterns were interpreted using data from the ICDD card index: powder diffraction database PDF2 (Powder Diffraction File) Release 2022 and diffraction patterns of minerals pure from impurities. For the main phases, the content was calculated. It can be seen that the ore contains dolomite \( \text{CaMg(CO}_3\text{)}_2 \); quartz \( \text{SiO}_2 \); pyrite \( \text{FeS}_2 \); sphalerite \( \text{ZnS} \); galenite \( \text{PbS} \). Figure 3 shows the derivatogram of the Shalkiya ore and its concentration tailings. Differential thermal analysis was performed on a Q-1000D MOM (Paulik-Erdey) Derivatograph (MOM company, Mateszalka, Hungary). Derivatogram recording conditions: operating range—from room temperature to 1000 °C; heating rate—from 0.6 to 20 °C/min; environment—air; automatic weight application; analysis sample—10 g; determination of thermal effects.
Figure 2. The Shalkiya ore’s X-ray diffraction pattern and results of the semi-quantitative X-ray phase analysis of crystalline phases.

It can be seen that the ore contains dolomite CaMg(CO₃)₂; quartz SiO₂; pyrite FeS₂; sphalerite ZnS; galenite PbS.

Figure 3 shows the derivatogram of the Shalkiya ore and its concentration tailings.

Differential thermal analysis was performed on a Q-1000D MOM (Paulik–Erdey) Derivatograph (MOM company, Mateszalka, Hungary). Derivatogram recording conditions: operating range—from room temperature to 1000 °C; heating rate—from 0.6 to 20 °C/min; environment—air; automatic weight application; analysis sample—10 g; determination of thermal effects.

(a) (b)

Figure 3. Derivatogram of the Shalkiya ore (a) and its concentration tailings (b). Name of curves: T-temperature, TG-change in sample mass (thermogravimetry), DTG-rate of mass change (differential thermogravimetry), DTA-curve of differential thermal.

Judging by the Shalkiya ore’s derivatogram (Figure 3a), the loss of the ore mass is 27.41%. Endothermic effects at 780 °C and 860 °C are associated with decarbonization of
dolomite. From Figure 3b, it follows that heating of the concentration tailings is accompanied by several endo-effects with minima at 152 °C, 792 °C, and 870 °C, accompanied by the mass loss. The total loss of the tailings’ mass at 1000 °C was 23.4%. The first endothermic effect is associated with dehydration of the sample, the second endo-effect with MgCO₃ decarbonization, and the third one with CaCO₃ decarbonization.

The Shalkiya ore and its concentration tailings and auxiliary materials were analyzed in the central analytical laboratory of the lead plant of LLP “A-MEGA TRADING”. Chemical titrimetric analysis (Trilon B, iodometric method) (ST RK 2853-16, ST RK 2854-16) was used to determine the main elements; the gravimetric method (GOST 13230.1-93) was used to determine silicon; the gas-volume method was used for sulfur and carbon; and sodium and potassium were determined in a flame photometric liquid analyzer PAZh-2.

The sulfide ore used for conducting the study has the following composition: ZnS—5.2%; PbS—1%; FeS₂—4.0%; SiO₂—50%; Al₂O₃—6.6%; CaCO₃—19.5%; MgCO₃—10.1%; Fe₂O₃—3.6%; Σ(Na₂O + K₂O)—0.7%. The concentration tailings of the Shalkiya deposit ore contain the following: ZnS—2.51%, PbS—1%, Fe—2.29%, Si—28.12%, S—1.28%, Ca—7.11%, Al—1.2%, Mg—2.63%. As a raw material containing Fe₃O₄, we used a magnetite concentrate produced at the Balkhash factory from copper ore flotation tailings [56], containing, in wt%, the following: Fe₃O₄—85.9; SiO₂—9.0; CaO—2; Al₂O₃—1.4; MnO—0.3; K₂O—0.3; Na₂O—0.2; MgO—0.4; ZnO—0.2; PbO—0.4. Coke contained 13.2% ash, 0.6% S, 0.4% H₂O, and 85.3% C. The steel shavings composition is 97.6% Fe, 1.8% C, 0.3% S, 0.2% Mn, and 0.1% of others. The composition of the initial mixture with the ore: tailings ratio = 1:1 is shown in Table 1.

### Table 1. Chemical composition of the mixture.

<table>
<thead>
<tr>
<th></th>
<th>ZnS</th>
<th>PbS</th>
<th>FeS₂</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaCO₃</th>
<th>MgCO₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>Na₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content%</td>
<td>3.3</td>
<td>0.8</td>
<td>2.0</td>
<td>55.6</td>
<td>4.6</td>
<td>18.8</td>
<td>9.5</td>
<td>4.5</td>
<td>0.3</td>
<td>0.6</td>
</tr>
</tbody>
</table>

### 3. Results and Discussion

The basis of the proposed method is the reaction:

\[
\text{ZnS + PbS + FeS₂ + Fe₃O₄ + 8SiO₂ + 12C} = \text{Zn(g) + Pb(g) + 4FeSi₂ + 4SO₂(g) + 12CO(g)}; \tag{1}
\]

which, from a thermodynamic point of view, can spontaneously occur (according to \(\Delta G^\circ = 0\)) at a temperature of >1877.15 °C (Table 2).

### Table 2. Effect of temperature on \(\Delta G^\circ\) *(kJ) of reaction 1.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>500</th>
<th>700</th>
<th>900</th>
<th>1100</th>
<th>1400</th>
<th>1600</th>
<th>1800</th>
<th>1877</th>
<th>1900</th>
<th>2000</th>
<th>2100</th>
</tr>
</thead>
<tbody>
<tr>
<td>3933.2</td>
<td>3332.6</td>
<td>2742.6</td>
<td>2160.9</td>
<td>1308.6</td>
<td>746.2</td>
<td>204.9</td>
<td>0</td>
<td>−60.71</td>
<td>−324.9</td>
<td>−588.3</td>
<td></td>
</tr>
</tbody>
</table>

* \(\Delta G^\circ\) was calculated using the Reaction Equations module of the HSC-6 software package.

The effect of temperature and amount of Fe₃O₄ on the silicon equilibrium distribution degree (aSi, %) is shown in Figure 4, and the zinc and lead distribution is presented in Table 3.
Figure 4. Effect of temperature and amount of magnetite on the equilibrium distribution degree of silicon-containing substances: amount of Fe$_3$O$_4$: (a) 38%, (b) 55%.

From Figure 4, it can be seen that the silicon-containing products formed at the SiO$_2$ reduction in the system are FeSi, Si, Fe$_3$Si, Fe$_5$Si$_3$, Fe$_{23}$Si$_{3}$, and SiO$_g$, which, based on the starting reduction temperature, form an increasing series: Fe$_3$Si (1200 °C); Fe$_5$Si$_3$, Si (1400 °C); and SiO$_g$, FeSi$_2$, Fe$_{23}$Si$_{33}$ (1500 °C). An increase in the amount of Fe$_3$O$_4$ reduces the extraction degree of silicon into its elemental state (for example, at 1800 °C from 14.21% to 3.16%), practically does not affect the transition degree of silicon to FeSi, and increases the transition degrees of silicon to Fe$_3$Si (from 2.56% to 7.14%) and Fe$_5$Si$_3$ (from 0.34% to 2.6%). However, in this case, the transition of silicon to FeSi$_2$ and Fe$_{23}$Si$_{33}$ is noticeably reduced.

An increase in the amount of Fe$_3$O$_4$ in the charge has a positive effect on the extraction of zinc into gas in the temperature range of 900–1600 °C (Table 3). However, at $T \geq 1700$ °C, regardless of the amount of Fe$_3$O$_4$, the transition degree of zinc into the gaseous state is more than 99%. A similar picture is observed with the influence of Fe$_3$O$_4$ on the transition degree of lead into gas in the temperature range of 1100–2000 °C. Lead in the system under consideration, despite the fact that lead is reduced at a lower temperature than zinc, passes into the gaseous state less completely than zinc. Even at 2000 °C, the transition degree of lead into gas does not exceed 92%.

To determine the optimal conditions for the joint electric smelting of the Shalkiya ore and its concentration tailings, further studies were carried out using the second-order rotatable planning designs (Box–Hunter plan) [57–59] followed (based on the regression
equation) by computer volumetric and planar images of the temperature and Fe$_3$O$_4$ effect on the extraction of silicon into the alloy—$\alpha_{Si(alloy)}$—and the silicon concentration in the alloy—$C_{Si(alloy)}$. The planning matrix and the research results are shown in Table 4.

**Table 3.** Effect of temperature and amount of Fe$_3$O$_4$ * on the equilibrium distribution degree of zinc- and lead-containing substances, %.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Temperature, °C</th>
<th>800</th>
<th>900</th>
<th>1000</th>
<th>1100</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
<th>1500</th>
<th>1600</th>
<th>1700</th>
<th>1800</th>
<th>1900</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnS</td>
<td>99.89 *</td>
<td>99.84</td>
<td>98.73</td>
<td>86.96</td>
<td>44.78</td>
<td>9.84</td>
<td>1.4</td>
<td>0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.12</td>
<td>0.10</td>
<td>0.15</td>
<td>0.21</td>
<td>0.13</td>
<td>0.04</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Zn</td>
<td>0.01</td>
<td>0.06</td>
<td>0.64</td>
<td>4.73</td>
<td>12.33</td>
<td>12.09</td>
<td>7.64</td>
<td>3.52</td>
<td>1.55</td>
<td>0.83</td>
<td>0.49</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>PbS</td>
<td>24.25</td>
<td>11.12</td>
<td>2.87</td>
<td>0.74</td>
<td>0.36</td>
<td>0.19</td>
<td>0.08</td>
<td>0.03</td>
<td>0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Pb</td>
<td>75.99</td>
<td>88.65</td>
<td>96.63</td>
<td>98.51</td>
<td>98.13</td>
<td>97.03</td>
<td>94.72</td>
<td>87.49</td>
<td>71.42</td>
<td>51.65</td>
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<td>Pb(g)</td>
<td>0.01</td>
<td>0.01</td>
<td>0.06</td>
<td>0.21</td>
<td>0.63</td>
<td>1.66</td>
<td>4.10</td>
<td>11.53</td>
<td>28.27</td>
<td>48.55</td>
<td>66.52</td>
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<tr>
<td>PbS(g)</td>
<td>0.17</td>
<td>0.62</td>
<td>0.85</td>
<td>0.94</td>
<td>1.28</td>
<td>1.53</td>
<td>1.50</td>
<td>0.7</td>
<td>0.21</td>
<td>0.07</td>
<td>0.03</td>
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<tr>
<td></td>
<td>0.22</td>
<td>0.99</td>
<td>1.65</td>
<td>1.94</td>
<td>2.68</td>
<td>3.22</td>
<td>3.50</td>
<td>2.81</td>
<td>1.78</td>
<td>0.82</td>
<td>0.41</td>
<td>0.28</td>
<td></td>
</tr>
</tbody>
</table>

(*) numerator—38% Fe$_3$O$_4$, (**) denominator—55% Fe$_3$O$_4$.

**Table 4.** Planning matrix and research results.

<table>
<thead>
<tr>
<th>#</th>
<th>Independent Factors</th>
<th>$\alpha_{Si(alloy)}$, %</th>
<th>$C_{Si(alloy)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>Coded Form</strong></td>
<td><strong>Natural Form</strong></td>
<td><strong>According to Research</strong></td>
</tr>
<tr>
<td>X1</td>
<td>X2</td>
<td>$T_r$, °C</td>
<td>Fe$_3$O$_4$, %</td>
</tr>
<tr>
<td>1</td>
<td>−1</td>
<td>1658</td>
<td>41.3</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>1941</td>
<td>41.3</td>
</tr>
<tr>
<td>3</td>
<td>−1</td>
<td>1658</td>
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<tr>
<td>4</td>
<td>1</td>
<td>1941</td>
<td>52.7</td>
</tr>
<tr>
<td>5</td>
<td>1.414</td>
<td>0</td>
<td>2000</td>
</tr>
<tr>
<td>6</td>
<td>−1.414</td>
<td>0</td>
<td>1600</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>1.414</td>
<td>1800</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>−1.414</td>
<td>1800</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>0</td>
<td>1800</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>1800</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>0</td>
<td>1800</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>0</td>
<td>1800</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>0</td>
<td>1800</td>
</tr>
</tbody>
</table>

#: This is number.
Based on the data in Table 4, we obtained the following adequate regression equations:

$$\alpha_{\text{Si(alloy)}} = -643.27 + 0.654 \cdot T + 2.766 \cdot \text{Fe}_3\text{O}_4 - 1.41 \cdot 10^{-5} \cdot T^2 - 5.23 \cdot 10^{-4} \cdot \text{Fe}_3\text{O}_4^2 - 1.58 \cdot 10^{-4} \cdot T \cdot \text{Fe}_3\text{O}_4$$  \hspace{1cm} (2)

$$C_{\text{Si(alloy)}} = 80.14 + 0.0845 \cdot T - 0.026 \cdot \text{Fe}_3\text{O}_4 - 3.1 \cdot 10^{-6} \cdot T^2 + 0.026 \cdot \text{Fe}_3\text{O}_4^2 + 1.085 \cdot 10^{-4} \cdot T \cdot \text{Fe}_3\text{O}_4$$  \hspace{1cm} (3)

The adequacy of Equations (2) and (3) is proven by the fact that the tabulated value of the Fisher criterion for the experimental error of ≤5 is equal to 6.59 [57]. It is greater than the calculated values of the Fisher criterion calculated for Equations (2) and (3).

The constructed volumetric and planar images of the temperature and Fe$_3$O$_4$ effect on $\alpha_{\text{Si(alloy)}}$ and $C_{\text{Si(alloy)}}$ are shown in Figure 5.

![Volumetric and planar images](image_url)

**Figure 5.** Volumetric (a) and planar (b) images of the temperature and Fe$_3$O$_4$ effect on $\alpha_{\text{Si(alloy)}}$ and $C_{\text{Si(alloy)}}$.

It can be seen that a high extraction degree of silicon into the alloy and a high concentration of this element in it is observed at high temperatures and a small amount of Fe$_3$O$_4$. The FeSi15 ferrosilicon is formed at relatively low temperatures in the $abc$ region (1600–1661 °C, 51.7%–55% Fe$_3$O$_4$), and FeSi25 ferrosilicon is formed in a wider temperature range (from 1600 to 1979 °C) in the presence of 42.8–55% Fe$_3$O$_4$—the $cdfa$ region. The FeSi45 grade of ferrosilicon can be produced in the $zht$ area at 1885–2000 °C in the presence of 39–39.7% Fe$_3$O$_4$. In this case, the extraction degree of silicon into the alloy is 70.9% (at point $z$)—75.4% (at point $t$, Figure 6).
The crucible. Such an unstable electric melting process is associated with the formation of gases in the system (CO, CO$_2$, Zn$_g$, Pb$_g$), which form a moving foam with the liquid melt. A similar phenomenon has been described repeatedly in pyrometallurgy [60,61]. The degree of foaming can be reduced by reducing the volume of gases in the system, for example, CO. For this purpose, we carried out the melting process by replacing some of Fe$_3$O$_4$ with steel shavings. The mode of inactive foaming of the melt was visually observed at more than 40%–60% replacement of magnetite’s iron with iron contained in steel shavings. Figure 6 shows a fracture of the crucible after the melting the ore and tailings mixture with 55% replacement of the magnetite concentrate’s iron with the steel shavings’ iron with a predicted silicon concentration in the alloy of 45%. The SEM analysis of the alloy is presented in Figure 7.

![Figure 6](image.png)

**Figure 6.** Photographs of the crucible fracture (a) and the resulting ferrosilicon (b).

The process of electric smelting of the ore and tailings mixture in the presence of magnetite concentrate and coke was accompanied by foaming with foam flowing out of the crucible. Such an unstable electric melting process is associated with the formation of gases in the system (CO, CO$_2$, Zn$_g$, Pb$_g$), which form a moving foam with the liquid melt. A similar phenomenon has been described repeatedly in pyrometallurgy [60,61]. The degree of foaming can be reduced by reducing the volume of gases in the system, for example, CO. For this purpose, we carried out the melting process by replacing some of Fe$_3$O$_4$ with steel shavings. The mode of inactive foaming of the melt was visually observed at more than 40%–60% replacement of magnetite’s iron with iron contained in steel shavings. Figure 6 shows a fracture of the crucible after the melting the ore and tailings mixture with 55% replacement of the magnetite concentrate’s iron with the steel shavings’ iron with a predicted silicon concentration in the alloy of 45%. The SEM analysis of the alloy is presented in Figure 7.

![X-ray spectra](image.png)

**Figure 7.** X-ray spectra of ferroalloy sample, obtained on SEM with EDS system and contents of elements by spectra.

The resulting ferrosilicon density (D) is 5.1 g/cm$^3$. The silicon content in the alloy, based on the dependence of $C_{Si(alloy)} = f(D)$, is 41.7% [62,63]:

$$C_{Si(alloy)} = 252.405 - 101.848D + 18.209D^2 - 1.243D^3. \quad (4)$$

An analysis was also carried out using the gravimetric method, which showed the silicon content in the alloy to be 42.1%. According to the silicon content (41.7%–42.1%), the ferroalloy smelted from the sulfide ore and tailings mixture, in accordance with [64], is ferrosilicon of FeSi45 grade.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Fe</th>
<th>Cr</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>2.33</td>
<td>41.9</td>
<td>55.13</td>
<td>0.31</td>
<td>0.33</td>
</tr>
</tbody>
</table>
A photograph of the operating electric furnace with sublimates deposited on the electric holder is shown in Figure 8a, the sublimates collected in the crucible in Figure 8b, and an SEM analysis of the sublimates in Figure 9.

![Figure 8](image)

Figure 8. Sublimates on the electric holder (a) and collected sublimates (b).

![X-ray spectra](image)

Figure 9. X-ray spectra of sublimates, obtained with SEM with EDS system and contents of elements by spectra.

<table>
<thead>
<tr>
<th>Element</th>
<th>Zn</th>
<th>Pb</th>
<th>Si</th>
<th>Cu</th>
<th>K</th>
<th>Fe</th>
<th>S</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>26.03</td>
<td>13.47</td>
<td>20.92</td>
<td>0.76</td>
<td>1.06</td>
<td>0.92</td>
<td>1.27</td>
<td>33.02</td>
</tr>
</tbody>
</table>

The resulting sublimates are a polymetallic zinc-lead oxide concentrate containing 26.03% Zn and 13.47% Pb. The zinc and lead content determined by chemical analysis is as follows: 26.15% Zn and 13.63% Pb.

The resulting sublimates can be further processed using the hydrometallurgical method with the zinc and lead products [65,66].

Therefore, the Zn content in the sublimates is 11.83 times greater than in the original mixture.

4. Conclusions

Based on the results of the thermodynamic study and experimental electric melting of a mixture of the Shalkiya lead-zinc sulfide ore and its concentration tailings in the presence of magnetite and coke, the following conclusions can be drawn:

1. Under equilibrium conditions:
   - The silicon-containing products of SiO₂ reduction are FeSi, Si, Fe₃Si, Fe₅Si₃, FeSi₂, FeSi₂, FeSi₂, and SiO₂, which, in accordance with the reduction starting temperature, form an increasing series: Fe₅Si₃ (1200 °C); Fe₃Si (1400 °C); and SiO₂, FeSi₂, FeSi₂ (1500 °C);
- The formation of low-silicon grades of ferrosilicon (FeSi15 and FeSi25) is possible at 1600–1979 °C in the presence of a large amount of magnetite (42.8%–55% of the mass of the ore and tailings mixture).

- The ferrosilicon of FeSi45 grade is formed in the temperature interval of 1885–2000 °C in the presence of the smaller amount of magnetite (39.7%); in this case, the silicon extraction degree into the resulting alloy is 70.9–75.4%.

2. Significant foaming, which becomes inactive when 40–60% of the iron in magnetite is replaced by the iron in steel shavings, is observed during electric smelting in the arc furnace of the mixture of the Shalkiya zinc-lead sulfide ore and its concentration tailings in the presence of magnetite concentrate and coke.

The electric smelting of the Shalkiya zinc-lead sulfide ore and its concentration tailings with the replacement of 55% of the iron in the magnetite concentrate with the iron in the steel shavings allowed us to produce ferrosilicon of FeSi45 grade (41.9%–42.1% Si) of which the silicon extraction degree was 85%, with sublimates containing 26.03% zinc and 13.47% lead with a zinc extraction degree of 97% and a lead extraction degree of 99%. In comparison with the initial mixture of ore and tailings, the obtained sublimates are 11.83 times richer in zinc.

Author Contributions: Conceptualization, V.S. and B.M.; methodology, V.S.; software, V.S.; validation, V.S., B.M. and D.A. (Dosmurat Aitkulov); formal analysis, V.S. and B.M.; investigation, V.S., B.M. and A.B.; resources, V.S. and D.A. (Dosmurat Aitkulov); data curation, V.S. and D.A. (Dosmurat Aitkulov); writing—original draft preparation, V.S. and B.M.; writing—review and editing, D.A. (Dosmurat Aitkulov), A.B. and D.A. (Daniel Amanov); visualization, A.B. and D.A. (Daniel Amanov); supervision, V.S.; project administration, B.M. and A.B.; funding acquisition, D.A. (Dosmurat Aitkulov). All authors have read and agreed to the published version of the manuscript.

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