INVESTIGATION OF AN ALUMINOTHERMIC SILICON SEPARATION FROM A CORUNDUM MATRIX

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ABSTRACT

The presented paper contains the research results of extraction of the reduced silicon from the corundum matrix by means of different methods. The research has been performed with use of several methods: separation in a heavy suspension, sedimentation in high-viscous mediums and electrostatic separation. The results obtained at the studying of separation of the matrix (corundum) and the silicon produced from quartz glass and aluminium powder allowed to draw following conclusions: separation in an alcohol-bromoform medium allows to take no more than 16% of silicon; in the process the silicon concentration in the product makes 40-42%; at use of a water-glycerine mixture the silicon content in the product makes 39-49%, and the extraction degree of Si in it is no more than 32%; electrostatic separation allows to extract into the product 83-89% of Si; in this case the product contains 88-92% of silicon; application of iodine transport (the “inverted crucible” technique) allows to produce high-pure (99%) silicon at the actual extraction of 72,5% and predicted one – 88,7%; for obtaining purer silicon (99,9999% of Si) we recommend to use vacuum purification.

Keywords: silicon, corundum matrix, heavy suspension, sedimentation, electrostatic separation.

INTRODUCTION

In world practice, there are known various methods of producing silicon of high purity¹-⁶. For example, obtaining silicon by purification of metallurgical silicon to the necessary purity, obtaining silicon from high purity quartz through its recovery and subsequent post-treatment methods using trichlorosilane and monosilane, with subsequent recovery or pyrolysis of silicon-containing intermediate compounds and obtaining polycrystalline silicon.

As we have noted in previous works, at the aluminothermic production of silicon from quartz glass and aluminium powder the silicon reduction degree in accordance with the reaction:

\[ 3SiO_2 + 4Al = 3Si + 2Al_2O_3 \]  

at 1260°C within 6 minutes makes 91%, and at 1300°C within the same time practically all the silicon is reduced⁷-⁸. The microscope studying has shown, that a great bulk of the reduced silicon (~60-65%) is in pores of a corundum matrix as particles with sizes of 0.01-0.5 mm and thin films rigidly bound with the matrix surface. For this reason, extraction of the reduced silicon from the matrix is sufficiently difficult. The presented paper contains the research results of extraction of the reduced silicon from the corundum matrix by means of different methods.

EXPERIMENTAL

The research has been performed with use of several methods: separation in a heavy suspension, sedimentation in high-viscous mediums and electrostatic separation. The separation in a heavy suspension has been realized with application of bromoform with density of 2.89 g/cm³.
The method is based on a difference between densities of Si (2.33 g/cm³) and Al₂O₃ (3.97 g/cm³). Before the separation, a corundum matrix and silicon had been ground to a fraction of 0.1-0.16 mm. A sample of the ground material (2 g) was placed in a graduated glass. Then 6 ml of the bromoform were added to the glass. After the first sedimentation of a heavy fraction (corundum) its volume was measured. Then the bromoform in the glass was diluted with a solvent (ethyl alcohol). At a performance of the research, we have used several alcohol-bromoform mixtures, which densities is represented in Table-1.

Table-1: Density of alcohol-bromoform mixtures.

<table>
<thead>
<tr>
<th>Vbf. %*</th>
<th>100</th>
<th>88</th>
<th>86</th>
<th>75</th>
<th>60</th>
<th>50</th>
<th>40</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>D, g/cm³°</td>
<td>2.89</td>
<td>2.55</td>
<td>2.50</td>
<td>2.43</td>
<td>2.16</td>
<td>1.86</td>
<td>1.69</td>
<td>1.32</td>
</tr>
</tbody>
</table>

Note: * – a volume fraction of bromoform; ° – the density of a liquid.

The bromoform, the sample and the alcohol were carefully mixed by a glass stick. After precipitation of a deposit, its volume was measured. The sedimentation and dilution stages were repeated from 3 to 5 times for obtaining of fractions with various densities within the limits of the density of the liquid, which was applied for the mixture separation.

For the implementation of the sedimentation analysis, a sample of the investigated powder with a fraction of 125 microns and weight of 2 g is placed in preliminary prepared measured cylinders and filled with a dispersive medium (water and glycerine), which total volume is 6 ml. Then the prepared suspension is carefully mixed. This analysis is realized by means of so-called a method of continuous determination of a sedimentation deposit. On the basis of experimental data, a curve of a phenomenological description of particles’ precipitation kinetics from time is constructed. A cinder on a filter after drying is analyzed by roentgen-phase techniques.

Electrostatic separation has been performed on a device ELKOR-1 (Russia). The separator is intended for separation of mixtures of loose materials with a grain of 0.1-5 mm differing by electric properties.

RESULTS AND DISCUSSION

The experiments with the use of bromoform allowed determining the optimum ratios of the alcohol and bromoform at which the greatest extraction degree of silicon from the corundum has been achieved. The silicon extraction degree has been determined by a roentgen-phase analysis of the obtained mixture at the use of a bromoform-alcohol mixture with a density of 2.5 g/cm³ and 2.55 g/cm³. Results of the roentgen-phase analysis of the top phase with the use of a bromoform-alcohol mixture with a density of 2.55 g/cm³ are represented in Fig.-1.

Fig.-1: Roentgen-phase analysis of a silicon-corundum mixture at the use of a bromoform-alcohol mixture with a density of 2.55 g/cm³.

The silicon extraction degree into a dry deposit – a concentrate – was no more than 16%. As a result of the eightfold separation of this deposit, we could obtain pure silicon (purity of 99.3%). At the work with
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bromoform, the yellow coloration of liquid layers over the charge has been noticed. This phenomenon is connected with the decomposition of bromoform under light and formation of hydrogen bromide and molecular bromine\(^9\-10\):

\[ CHBr_3 \rightarrow HBr + Br_2 \quad (2) \]

Silicon and corundum can react with HBr and Br\(_2\) giving different by-products (SiBr\(_4\), AlBr\(_3\), HBr, etc.), which complicate the Si-Al\(_2\)O\(_3\) separation process.

Low indicators of the separation in a bromoform medium are also connected with the fact that a basic part of the obtained silicon represents the fine-dispersed particles and films closely bound with the matrix. Their removal demands very thin grinding. However, in this case, a difference between the silicon and corundum densities is imperceptible, that leads to a stop of the separation process. Therefore, the separation of the matrix from the silicon with use of a bromoform-alcohol mixture is not an optimum variant. For the Si-Al\(_2\)O\(_3\) separation from a fine-dispersed material, it is suggested to apply a viscous medium, for example, glycerine.

At the implementation of experiments in a water-glycerine mixture, we have determined a ratio of the deposit volume (V) to the suspension total amount (V\(_o\)). On the basis of these data dependences of \(V/V_o = [\gamma]\) on time and viscosity of a dispersive medium have been constructed (Fig.-2).

![Figure-2](image)

FIG.-2: Effect of a dispersive medium’s viscosity and sedimentation time of solid particles on [\gamma].

By reason of a complex character of viscosity influence on [\gamma] in intervals of 0,018-0,031 Pa·s and 0,1-0,12 Pa·s we have applied a rotatable second-order method of planning an experiment\(^11\-12\). The experiments, connected with studying the joint influence of viscosity and time on [\gamma], have been carried out for two above-stated viscosity intervals. The planning matrix and obtained results are represented in Tables-2 and 3.

The equations 1, 2 have been applied for construction of three-dimensional response surfaces and their horizontal sections (Fig. 3). Figure 4 is a photo of the cylinders, which have been used for the separation of corundum from silicon at different densities of water-glycerine mixtures.

At a viscosity of 0,12 Pa·s the corundum deposit becomes denser. At the same time in the volume over the dense Al\(_2\)O\(_3\) deposit, there is the formation of a suspension of easier silicon (Fig. 4). The formation conditions of the dense Al\(_2\)O\(_3\) deposit (at [\gamma] \(\leq 0,2\)) and the silicon suspension can be determined from Fig. 3, according to which u should be within 0,117-0,12 Pa·s and sedimentation time from 10 to 60 minutes, and for [\gamma] from 0,15 to 0,152 the suspension viscosity makes 0,119-0,12 MPa and sedimentation time 45-60 minutes.
For effective extraction of silicon from this suspension we have carried out the experiment, which combines sedimentation and flotation processes. For this purpose, a bubbling, controlling a quantity of fed bubbles, is placed in a quartz vessel. The bubbles form a pulp-air mixture, lift the powder from the bottom and, ipso facto, promote fuller separation of heavy particles. Figures 5 and 6 show the formation of air-silicon bubbles on a surface of the water-glycerine mixture with the subsequent extraction of silicon. Silicon content in a dry powder of the top phase makes 39-49%. However, the silicon extraction degree into the top phase is only 24-32%.

<table>
<thead>
<tr>
<th>Variables</th>
<th>Natural kind</th>
<th>$V_0/V_{c} = \frac{\mu}{\gamma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x_1$</td>
<td>$x_2$</td>
<td>[mi], Pa·s</td>
</tr>
<tr>
<td>+</td>
<td>+</td>
<td>0.03</td>
</tr>
<tr>
<td>-</td>
<td>+</td>
<td>0.02</td>
</tr>
<tr>
<td>+</td>
<td>-</td>
<td>0.03</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>1.41</td>
<td>0</td>
<td>0.032</td>
</tr>
<tr>
<td>-1.41</td>
<td>0</td>
<td>0.018</td>
</tr>
<tr>
<td>0</td>
<td>1.41</td>
<td>0.025</td>
</tr>
<tr>
<td>0</td>
<td>-1.41</td>
<td>0.025</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0.025</td>
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<tr>
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<tr>
<td>0</td>
<td>0</td>
<td>0.025</td>
</tr>
</tbody>
</table>

On the basis of the data (Table-2 and 3) following adequate regression equations have been obtained:

\[
\gamma(0.018-0.032) = 0.11 + 1.751 \times \mu - 1.705 \times 10^{-3} \times \tau - 3.285 \times 10^{-7} \times \tau^2 - 2.285 \times \mu \times \tau \quad (3)
\]

\[
\gamma(0.1-0.12) = 5.166 + 105.209 \times \mu - 1.168 \times 10^{-3} \times \tau - 5.052 \times \mu^2 - 9.62 \times 10^{-7} \times \tau^2 + 0.012 \times \mu \times \tau \quad (4)
\]
I – $[\eta] = 0,018 - 0,03$ Pa·s; II – $[\eta] = 0,1 - 0,12$ Pa·s; 
the numerals on the lines – $V/V_0 = [\gamma]$

Fig.-3: Time and viscosity effect on a $V_0/V_c$ ratio.

Fig.-4: Matrix-silicon separation pictures for viscosity of a water-glycerine mixture of $0,018$ Pa·s (1), $0,025$ Pa·s (2), $0,11$ Pa·s (3) and $0,12$ Pa·s (4).

Fig.-5: Formation of air-silicon bubbles.

Fig.-6: Distribution of silicon on the liquid surface.

The analysis of the top phase of the foam formed on a surface of the water-glycerine mixture is represented in Fig.-7.
For reduction of a quantity of the fine-crystalline silicon particles closely bound with the simultaneously formed corundum matrix, it is necessary to organize such the process, when the silicon and the corundum will be formed non-simultaneously. With this end in view, we have carried out the experiments in accordance with the technique of inverted crucible suggested by Digonsky\textsuperscript{13} for studying of reactions with use of gaseous hydrogen. The problem consists in using of gas transport during the reduction process and obtaining silicon in one stage with its simultaneous purification. Realization of the reduction reaction in a closed crucible allows organizing counter-current flows of iodine and silicon iodides\textsuperscript{7}.

In this case the silicon sedimentation in the top part occurs not at the expense of reduction but owing to the reaction: $\text{SiI}_4 \rightarrow \text{Si} + 2\text{I}_2$. Therefore, such the silicon is not fixed rigidly in a corundum matrix. The given experimental technique is described in\textsuperscript{14}. In addition, we have performed experiments with a sample of a pelleted charge with the weight of 1000 g (625 g of quartz glass and 375 g of an aluminium powder). The charge pellets after roasting have been ground to a size of 1 mm and loaded in a crucible with the addition of 3 g of iodine. Then the charge is heated in a non-isothermal regime to a temperature of 1850 K in the top part within 10 minutes. Microscopic studying has shown that the most part of the silicon has no rigid fastening with corundum and represent the fine (10-20 microns) particles and globules located in pores of the sintered material. A technology of this process and material flows are represented in Figure 8 from which follows, that 625 g of quartz glass (290,21 g of Si) give 212,5 g of enriched silicon (210,38 g of Si).

Thus, the silicon extraction degree into the product is 72,5%. The silicon losses (27,5%) are connected with the laboratory equipment imperfection, in particular, 16,2% of Si (47,5 g) have been lost with a dust-like phase at the mechanical size grading failing necessary dust removal equipment. Therefore, the actual output of the end product (purity of 99%) makes 88,7%. A silicon with purity of 99,9999% (6N) can be obtained by vacuum cleaning\textsuperscript{15-19}. With a purpose of electrostatic separation of the matrix from the reduced silicon the briquettes after the thermal processing have been ground to fraction < 500 microns. After processing in a device ELKOR-1 it has been established, that an electroconductive fraction makes 29-30%, and a non-electroconductive fraction – 70-71%. The microscopic analysis has shown that the electroconductive fraction is mainly composed of silicon globules and scales. Some scales are fixed with the corundum. The spectral analysis of the fraction has shown that silicon content is 88-92% and aluminium oxide content is 8-12%. The experiments have shown that the silicon extraction degree from the matrix makes 83-89% that exceeds industrial indicators of existing technologies in several times.

**CONCLUSION**

The results obtained at the studying of separation of the matrix (corundum) and the silicon produced from quartz glass and aluminium powder allowed to draw the following conclusions:

- separation in an alcohol-bromoform medium allows to take no more than 16% of silicon; in the process, the silicon concentration in the product makes 40-42%;
at the use of a water-glycerine mixture, the silicon content in the product makes 39-49%, and the extraction degree of Si in it is no more than 32%.

- electrostatic separation allows to extract into the product 83-89% of Si; in this case, the product contains 88-92% of silicon;
- application of iodine transport (the “inverted crucible” technique) allows to produce high-pure (99%) silicon at the actual extraction of 72.5 % and predicted one – 88.7%; for obtaining purer silicon (99,9999% of Si) we recommend to use vacuum purification.

**Fig.-8: Technological scheme of enlarged experiments.**

**ACKNOWLEDGMENT**

This work was supported by the Ministry of Education and Science of the Republic of Kazakhstan for grant financing on the theme Development of aluminothermy method of silicon receiving of "solar" purity (6N).

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[RJC-2038/2018]