Studies various factors effecting the synthesis of submicron silicon dioxide particles by leaching from waste dumps of the Balaklavskoe deposit

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Abstract. The paper presents the results of studies of the main parameters of synthesis of silicon dioxide powder from Balaklava deposit sludge with silicon dioxide content of 24%. During the study caustic soda solution is used as a leaching agent and sulfuric acid was used as a precipitant. At the leaching stage the concentration of leaching agent, the ratio of liquid phase to solid phase, the optimum temperature of leaching as well as the mode of pulp agitation are investigated. At the precipitation stage, the following parameters are considered: concentration of precipitating agent and temperature of the precipitation process. As a result of using the optimal parameters the high efficiency of obtaining silica powder of 98.56% is achieved. Average particle size is 200-800 nm, and agglomerate size is more than 800 nm.

1. Introduction

Every year more than hundreds of thousands of tons of silicon dioxide are produced in the world. However, the demand for this type of products is constantly growing, and energy- and resource-intensive technologies are required to meet it. The high consumption of silica is justified by a wide range of its applications in construction, chemical, rubber, medical and other industries [1–2]. The greatest demand for silica is observed in the construction industry, which is associated with the possibility of using it as a filler to improve the strength, corrosion and other properties [3–4] of building materials (cement, dolomite binders [5–9], glass and carbon plastics, rubber, insulation materials). The use of nanosized silica allows significantly expanding the field of its application [10–12]. Thus, the development of nanoscale silica production technology and the choice of optimal parameters for these technologies is an actual problem today.

One of the main problems of any production is the limited amount of raw materials and the presence of large amounts of waste materials. Both natural raw materials and silica-enriched industrial wastes such as rice hulls, bauxite, diatomite, apatite, etc. are used as raw materials for silica production [13–14]. Each of them has certain disadvantages and creates difficulties in the production process: the high cost of raw materials, their limited availability, the presence of hardly separable components, unfavorable costs of reagents, which creates a need to search and develop technologies that use more accessible raw materials.

With the constant development of the mining, construction and metallurgical industries, the volume of quarry waste is increasing, the growth and accumulation of which represent a certain environmental problem. The authors propose a way of using such waste as a raw material for production of silicon dioxide. In our opinion, the use of quarry waste in the technology of silica production will effectively...
utilize the dumps with the extraction of valuable component and significantly reduce the cost of its production.

Samples from the Balaklavskiy quarry dumps were used as raw materials containing silicon dioxide. Earlier studies were conducted on the effect of the main parameters of silica synthesis on the efficiency of the process using the waste dumps of the Psilerakh deposit as a raw material. The difference of this work is the use of waste as raw materials, with the concentration of silica in it being more than 2 times lower than in the samples studied in the previous work. The content of silica in the samples of this deposit is 24%.

The elemental composition of the sample was carried out on the analytical complex on the basis of vacuum X-ray fluorescence crystal diffraction scanning spectrometer “SPEKTROSCAN MAX – GVM” produced by SPEKTRON, Russia. The composition of the feedstock is presented in Table 1.

| Analit | Unit | Value  |
|--------|------|--------|
| MnO    | mg/kg| 409.169|
| V      | mg/kg| 129.156|
| Co     | mg/kg| 15.827 |
| Ni     | mg/kg| 37.325 |
| Cu     | mg/kg| 12.117 |
| Zn     | mg/kg| 95.149 |
| As     | mg/kg| 1.918  |
| Sr     | mg/kg| 96.3   |
| MgO    | %    | 1.904  |
| Al₂O₃  | %    | 15.65  |
| SiO₂   | %    | 24.214 |
| P₂O₅   | %    | 0.090  |
| K₂O    | %    | 4.818  |
| CaO    | %    | 14.505 |
| TiO₂   | %    | 0.952  |
| Fe₂O₃  | %    | 6.958  |

The microstructure of the silica powder was studied using a Phenom Pro X scanning electron microscope with EDS microanalysis (Phenom-World BV, the Netherlands). Silica particle size analysis was determined using Phenom's Element Identification program.

The proposed method of obtaining silica powder involves two main stages: leaching of silica from the original sample, converting it into soluble sodium metasilicate and precipitation of silica from solution using mineral acid.

To identify the optimum conditions affecting the main stages of silica production a number of studies were conducted:

- at the leaching stage: determining the concentration of leaching agent (caustic soda), ratio of liquid phase to solid phase, leaching temperature, and stirring speed;
- at the precipitation stage: determining the concentration of precipitant (sulfuric acid) and precipitation temperature.
2. Analysis of the research results

The results of the study (Fig. 1) of the effect of sodium hydroxide concentration on the degree of leaching show that the leaching efficiency increases with increasing concentration of leaching agent. The maximum efficiency is observed when caustic soda concentration of 40 wt.% is used.

![Figure 1. Effect of NaOH concentration (wt.%) on the degree of SiO\textsubscript{2} leaching.](image)

Based on the results of the study of the leaching efficiency dependence on the ratio of liquid phase to solid phase (fig. 2), we can see that the leaching degree increases with increasing ratio. The minimum effective result is obtained at a ratio of 2:1 and amounts to 19.4 % of leaching. The maximum efficiency is observed at a ratio of 20:1 and amounts to 32.8%.

![Figure 2. Effect of L:S ratio on the degree of SiO\textsubscript{2} leaching.](image)

An important parameter that significantly affects the leaching process is the temperature regime. The results of the study (Fig. 3) show that when leaching is carried out for 5 hours at 800°C, the process proceeds with 31.4% efficiency, and at 1100°C the silicon dioxide leaching efficiency increases more than 1.4 times.
Figure 3. Influence of temperature on the degree of SiO\textsubscript{2} leaching.

The results of the study of the relationship between the degree of leaching and stirring speed (Fig. 4) show that the maximum is achieved when using a stirring speed of 800 rpm, a further increase in the number of revolutions has no effect on the change in efficiency.

Figure 4. Dependence of SiO\textsubscript{2} leaching degree on stirring speed.

The efficiency of silica production depends on the precipitation parameters. One of the important parameters is the concentration of precipitating agent. Based on the results of the study (Fig. 5, a), with increasing concentration of sulfuric acid the degree of silica deposition decreases. The maximum SiO\textsubscript{2} precipitation effect of 93\% is observed at H\textsubscript{2}SO\textsubscript{4} concentration of 10 vol.\%.
Figure 5. Influence: a) of acid concentration on the degree of SiO$_2$ extraction; 
b) of temperature on the degree of SiO$_2$ extraction.

The results of the effect of temperature on the deposition process (Fig. 5, b) shows that with increasing temperature the efficiency of silica deposition decreases. The maximum degree of SiO$_2$ extraction is observed at 25°C and is 93%.

As a result of using the optimal parameters selected during the study, silica powder is synthesized (Table 2).

Table 2. Elemental analysis of the silicon dioxide powder under study/

| Analit  | Unit    | Value  |
|---------|---------|--------|
| MnO     | mg/kg   | 33.969 |
| V       | mg/kg   | 2.065  |
| Co      | mg/kg   | 0.583  |
| Ni      | mg/kg   | 4.270  |
| Cu      | mg/kg   | 11.239 |
| Zn      | mg/kg   | 20.369 |
| As      | mg/kg   | 0.677  |
| Sr      | mg/kg   | 10.659 |
| MgO     | %       | 0.144  |
| Al$_2$O$_3$ | %   | 0.762  |
| SiO$_2$ | %       | 98.558 |
| P$_2$O$_5$ | %   | 0.065  |
| K$_2$O  | %       | 0.275  |
| CaO     | %       | 0.048  |
| TiO$_2$ | %       | 0.056  |
| Fe$_2$O$_3$ | % | 0.056  |
Microphotographs of silicon dioxide powder at different magnifications are shown in Fig. 6. The powder represents particles and agglomerates of particles. The images (Fig. 7c and d) clearly show that the surface of the particles is covered with pores of different sizes on the micro- and nanometer scale.

![Microstructure of silicon dioxide powder at different magnifications.](image)

**Figure 6.** Microstructure of silicon dioxide powder at different magnifications: a) x 2000 times; b) x 5000 times; c) x 15000 times; d) x 20000 times.

The particle size of the synthesized silica ranges from 271 nm to 2.13 μm (Fig. 7).

![Particle size distribution of SiO₂ powder.](image)

**Figure 7.** Particle size distribution of SiO₂ powder.
Conclusions
As a result of the study the optimum process parameters have been selected for the production of silica from waste dumps:

- for the leaching process: concentration of leaching agent NaOH of 35 wt.%; ratio L:S of 20:1; leaching temperature of 110°C; and stirring speed of 800 rpm;
- for the precipitation process: concentration of the precipitating agent H₂SO₄ of 10 vol.%; and precipitation temperature of 25°C.

As a result of selection of optimal conditions the submicron powder of silicon dioxide with purity of 98.56% has been obtained. Quarry spoil with low content of bound silica was used as a raw material. The research shows the possibility of using raw materials with low silica content, so we can conclude about the universality of this method for obtaining the product from various waste dumps. For example, the leaching temperature is reduced to 110°C in contrast to previous results. Increasing the stirring speed to 800 rpm serves to obtain a higher degree of leaching. Overall, the proposed approach is shown to be applicable to the extraction of silicon with initial contents ranging from 24.2 to 52.16, which in turn indicates the versatility of the silicon extraction method.

In further studies it is planned to consider the influence of hydrocavitation and ultrasonic cavitation on silica extraction processes and lyophilic drying on the parameters of silica particles.

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