Structure of Enriched Ultradisperse Wastes of Silicon Production and Concretes Modified by them

V V Kondratiev¹, A I Karlina², E A Guseva³, M V Konstantinova⁴ and V O Gorovoy⁵
¹ Head of the Innovation and Technology Center, Irkutsk National Research Technical University, 664074, Russia, Irkutsk, Lermontov street, 83
² Deputy Head of the Innovation and Technology Center, Irkutsk National Research Technical University, 664074, Russia, Irkutsk, Lermontov street, 83
³Ph.D., Associate Professor of the Chair of Machine-Building Technologies and Materials, Irkutsk National Research Technical University, 664074, Russia, Irkutsk, Lermontov street, 83
⁴ Ph.D., Associate Professor of the Chair of Machine-Building Technologies and Materials, Irkutsk National Research Technical University, 664074, Russia, Irkutsk, Lermontov street, 83
⁵ Lead Engineer of the Innovation and Technology Center, Irkutsk National Research Technical University, 664074, Russia, Irkutsk, Lermontov street, 83

E-mail: karlinat@mail.ru

Abstract. Mainstreaming into practice of high-tech research methods allows to conduct deeper studies of the structure of materials when changes in them occur at the molecular level. The development of technologies for obtaining materials characterized by ultrafine structure is a promising direction, since it allows to obtain materials with higher properties. Use of the products, that are waste products of silicon production, for this purpose will allow to unload the sludge dumps and reduce the environmental load. During the research, method of scanning electron microscopy was used in work, its high efficiency was confirmed due to the high speed of the analysis, short preparation time, possibility of determining the composition of the substance. Untreated wastes, as well as the products of their processing with the use of flotation, were studied, characteristics of their structure are given. Product of processing with a high content of silicon was used as a modifier of concrete. Structure of concrete was studied before and after the modification, reasons for the increase in strength were explained.

1. Introduction
Solution of the problems of modern material science - development and use of new materials, improvement of processing methods with an aim to improve the operational characteristics of materials - is inextricably linked with the development of modern methods of studying the structure of matter. Traditional methods for studying the structures of metals and alloys are not applicable for the study of materials with ultrafine grains, since they do not allow to obtain detailed information on their structure. Active introduction of high-tech research methods into practice allows to conduct a deeper study of the structure when changes occur at the near-molecular level. Use of ultradisperse materials in...
various fields should consider the new properties of materials that they exhibit in connection with the developed surface.

The relevance and scientific significance of the issue with a brief literature review. Researchers should have an arsenal of tools that allow to register a structure, analyze it, make the necessary manipulations. Modern methods of research have their pros and cons.

Atomic force microscopy is a type of probe microscopy, based on the exchange interaction of probe atoms and the studied sample [1]. With the help of an atomic force microscope it is possible to study the friction, elasticity, adhesion, and also to move individual atoms, to precipitate and remove them from any surface. The drawbacks of this method include the complexity of setting up and preparing the probe for the study, the duration of the process, and the inability to determine the composition of the test substance.

X-ray types of analysis are good for their relatively low cost, they allow you to determine the chemical composition and types of compounds that make up the sample, but it is impossible to determine the particle size, their morphology, and it is also impossible to manipulate the substance.

Electron microscopy is based on the use of a directed electron beam, is divided into transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The first version is an energy-consuming and very labor-intensive method with a complex sample preparation process, which allows to obtain only visual information about the sample.

Scanning electron microscopy makes it possible to obtain several types of data about a sample - topology of the surface, elemental analysis, and the situation picture of the distribution of elements over the surface of matter. The process of sample preparation is quite simple, it is possible to study a wide range of materials - with the exception of liquids, gases, colloidal systems. There is a wide range of methods for researching materials. It is possible to perform several operations, which allows to carry out a number of studies at once [2-4].

The choice of the method of investigation is determined, of course, by the availability of the necessary equipment.

However, from the point of view of a complex study of ultradisperse materials, scanning electron microscopy is very attractive.

The production of ultradisperse materials requires special technologies, which are very energy-intensive. It has been suggested that a number of manufacturing processes, in particular metallurgical ones, that consume a huge amount of energy, can be accompanied by the production of substances with a high degree of dispersion, including those that are waste products. Thus, technogenic wastes of silicon production are dust of gas scrubbing of waste gases of electrothermal silicon production in ore-thermal furnaces. This product is formed during evaporation in the high-temperature zone (can reach 5000 °C in the arc melting zone) and subsequent condensation of sublimations. The calculations and results of laboratory studies showed that practically all quartzite carried away in the form of a fine fraction into the gas removal system during the production of silicon is represented in the form of micro- and nanospheres of SiO2 [5,6,7].

The processing of silicon production wastes with the help of flotation allows to obtain product enriched in silicon [8-11]. To date, detailed studies of separation products have not been carried out. The study of the application of waste products as modifiers of concrete showed that this makes it possible to increase its strength characteristics [12].

2. Research objective
The purpose of this work was to develop a methodology to study samples of waste products from silicon production using scanning electron microscopy, as well as to study the structure of concretes obtained by modifying them with these products.

3. Results of experimental studies
At present, gas scrubbing dust of electrothermal furnaces of silicon production of such large enterprises as the Irkutsk Aluminum Smelter is sent to the sludge dumps. The composition of dust
includes silicon oxide, carbon and other impurities. The results of investigations of untreated sludge, carried out with the help of scanning electron microscopy (Figure 1), confirmed the assumptions about the structure of the slurry [5,6,7].

Microscopes equipped with an ion gun allow to "cut" an interesting structural element. This operation allowed to determine that the microsphere of silicon oxide, which image in the foreground, is hollow inside (Figure 1, a). A more detailed study demonstrated the presence of conglomerates of spherical particles of SiO$_2$ and carbon nanotubes in the sludge (Figure 1, b).

In the course of the research, technique for studying samples of waste processing products obtained by flotation (Figure 2), foam product with a high content of carbon and flotation tail with an increased content of silicon oxide.

In the structure of the foam product (Figure 2, a), conglomerates of carbon nanotubes and spherical micro- and nanocrystalline SiO$_2$ are observed. The structure of the flotation tail is mainly represented by micro- and nanospheres SiO$_2$ in Figure 2, b).

The use of scanning electron microscopy and X-ray microanalysis made it possible to significantly facilitate and accelerate the development of separation technology. For example, when studying the process of removing carbon from foam product and flotation tail product during annealing, obtained result could be observed visually. Such an observation showed that the concentration of carbon particles decreased with increasing time and annealing temperature.

Further processing of the flotation tail [9-11] allowed to obtain a modifier, which in further studies was used as an additive to concrete [13-16].

Study of the obtained concrete samples by the methods of scanning electron microscopy required a certain sample preparation, since this material is inherently dielectric. Under the influence of
accelerated electrons, samples begin to accumulate a static charge, which adversely affects the quality of the images. To obtain high-quality images, a thin layer of gold, several angstroms thick, was deposited on the surface of the samples after preliminary cleaning, degreasing and drying, sufficient to remove the static charge and obtain the required quality of image obtained in secondary electrons.

The structure of the sample of concrete without additives (Figure 3) represents a typical structure of concrete, when sufficiently structurally coarse hydration products in the form of plates, flakes, fibers, needle-shaped crystals are located on the surface of cement grains (Figure 3, a). They practically don't influence the degree of filling of cracks between the cement grains (Figure 3, b), which can be formed as a result of shrinkage of cement stone.

![Figure 3. Structure of concrete without modifying additives.](image)

Also, cracks can form due to a loose approach of cement particles in case if products of hydration are not enough to fill them. Such porosity has a negative effect on the strength characteristics, since the structure is formed from crystallites of different sizes, unable to completely fill the cracks that enter the microscopic level by the classification of the structure of cement stone by the level of dispersion [17-20].

The structure of the sample of concrete with the optimum addition of a modifier in an amount of 9% of the mass of the cement looks different (Figure 4).

![Figure 4. Structure of concrete obtained with the use of the modifier.](image)
cracks (Figure 4, b). Probably, observed hardening of samples of modified concrete more than twofold can be due precisely to the denser packing of neoplasms in the structure of modified concrete [13-16].

4. Conclusions
1. High efficiency of scanning electron microscopy was demonstrated during the research due to the high speed of the analysis, short preparation time, possibility of determining the composition of the substance.
2. Using this method, the analysis of wastes of silicon production, as well as products of their processing by flotation, was carried out.
3. Effect of the modifier on the structure of concrete was studied.
4. On the basis of the comparative analysis of the structure of concrete without additives and the modified one, effect of the modifier on the strength increase is explained.

5. References

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