Comparative Analysis of the Principal Characteristics of Microsilica Obtained from Silicon Manufacture Wastes and Used in Concrete Production Technologies

V B Balabanov, K N Putsenko
Department of Urban Construction and Management, Irkutsk National Research Technical University, 83, Lermontov St., Irkutsk 664074, Russia

E-mail: putsenko_kseniya@mail.ru

Abstract. On the basis of the survey of foreign and domestic literature over the past 65 years devoted to the study of the properties and the technology of applying microsilica in the capacity of modifying additives to concretes. Microsilica obtained as a by-product from the waste of ferroalloy plants and from the plants involved in production of silicon compounds is discussed. Analysis of the principal characteristics of different types of microsilica obtained from different sources is conducted.

1. Introduction
The XXI century is characterized by extensive development of the construction industry on the basis of contemporary understanding of material science. Construction material science sets the objectives bound up with the elaboration of increasingly advanced technologies of building materials production characterized by improved exploitation characteristics under the condition of minimization of raw material, energy and labor costs. Concretes are the most common types of building materials. Their performance depends dependent to a large extent on the cement used, the composition and such properties of the aggregate as density, strength, aggregate gradation and adhesion.

Practice has given evidence that in the process of elaboration of cement concretes is the capacity of modifier, it is rational to use microsilica (MS), since it provides for improved performances with respect to strength, mobility of the mixture, permeability (for water and gases) and frost resistance. In this connection, it is expedient to conduct comparative analysis of the principal characteristics of the MS, obtained from silicon manufacture wastes and used in concrete production technologies.

The objective of the present study consists of (i) comparative assessment of the MS modifying properties in course of production of high-strength concretes with the orientation to identification of the concretes characterized by enhanced anti-corrosive and frost-resistant properties. The essential characteristics of the investigation increases due to the need in elaboration of a wide range of mix formulations (compositions) for high-strength concretes with special properties.

The goal of the study presumes formulation of a concrete production technology characterized by low corrosion properties.

The main cause of destruction of the concrete with MS addition is bound up with corrosion, which is formed due to icing or sea salts. Hence one of the main goals presumes making concrete sulfate-resistant.
2. Microsilica as a technological product

Microsilica is a by-product of silicon and ferrosilicon manufacture. MS is formed as a result of oxidation monoxide SiO formed in the process of (i) melting of silicon-containing alloys in electric arc furnaces in the gas phase by condensation of SiO₂ microparticles from the gas phase and (ii) their extraction from furnace gases. After oxidation and condensation, some part of SiO₂ forms small spherical particles with an increased content of amorphous silica [1-4]. Thus, the MS consists mainly of MS of amorphous (non-crystalline) silicon dioxide (SiO₂).

One of the most rational applications of MS is adding it to concrete. During the latter 30-40 years, extensive study of ultradisperse mineral silicon additives to concrete characterized by a high content of SiO₂ and providing for improved strength and frost resistance has been carried out. The development of technologies for the production of concretes with additives MS in the concrete mix has become the result of this study. But only since the 1990s, MS was recognized by the world community as an additive to concrete, which provides for improved properties of both freshly mixed mixture and hardened concrete. The latter is bound up with the fact that individual particles of SiO₂ are extremely small: these have a size of about 1 / 100th of the average particle size of the cement. Due to the small size of the MS particles and the high SiO₂ content, MS as pozzolan acquires larger reaction efficiency when used in concrete [4-8].

3. Performing a comparative analysis of microsilica

There are 5 plants producing ferroalloys and silicon compounds on the territory of Russian Federation: Kuznetsk Ferroalloys, Ltd., Chelyabinsk Electrometallurgical Plant, Ltd., Serov Ferroalloy Plant, Ltd., Bratsk Ferroalloy Plant, Ltd., Kremniy (Shelekhov) RUSAL, Ltd.

We have performed a comparative analysis of the principal characteristics (chemical composition) of microsilica of these manufactures. The respective data are presented in Table 1.

Table 1. Performing a comparative analysis of microsilica of several manufactures.

| Manufacture name | Intention | Class | Chemical composition |
|------------------|-----------|-------|----------------------|
| **Elkem Microsilica®**<br>Grade 920<br>ASTM (Norway) | For concretes and construction solutions | Class 920 is available in the two forms: unsealed (920 U), bulk density, which is usually 200–350 kg / m³; and pressed (920 D), bulk density – 500–700 kg / m³ | SiO₂ : 85-90%; SO₃ : 1-2%, Cl : 0.1-0.3%, CaO : 1.0%, Si : 0.2-0.4%, Na₂O : 1-1.5%, C : 1.5-2.0% |
| **Kuznetsk Ferroalloys, Ltd.**<br>For obtaining concretes with special properties: ultrahigh-strength, improved (i) frost, (ii) sulphate and (iii) corrosion resistance, watertightness | Unsealed – MS-85, MS-65; Compacted - MSC-85, MSC-65; In the form of a suspension - ISS-85 | SiO₂: 90-92%; Al₂O₃: 0.6-0.8%; Fe₂O₃: 0.4-0.7%; CaO: 0.4-0.9%; MgO: 0.8-1.0%; Na₂O: 0.6-0.8%; K₂O: 1.2-1.4%; C: 0.9-1.2%; S: 0.2-0.3% |
| **Chelyabinsk Electrometallurgical Plant, Ltd.**<br>Additive to concrete for improved performance | Unsealed - MS-85, MS-65; Compacted - MSC-85, MSC-65; In the form of a suspension - ISS-85 | SiO₂: 90-92%; Al₂O₃: 0.6-0.8%; Fe₂O₃: 0.4-0.7%; CaO: 0.4-0.9%; MgO: 0.8-1.0%; Na₂O: 0.6-0.8%; K₂O: 1.2-1.4%; C: 0.9-1.2%; S: 0.2-0.3%. |
b)

Serov Ferroalloy Plant, Ltd. Additive to concrete, for improved performance FS65, FS45

ΦС65 (Si: 63-68%, C: 0.1%, S: 0.02%, P: 0.05%, Al: 2.5%, Mg: 0.4%, Cr: 0.4%)

ΦС45 (Si: 41-47%, C: 0.2%, S: 0.02%, P: 0.0%, Al: 2.0%, Mg: 1.0%, Cr: 0.5%)

Bratsk Ferroalloy Plant, Ltd. Additive to concrete, which is widely used in the manufacture of classes of concrete subject to erosive abrasion and possessing improved water resistance FS65, FS75

ΦС65 (Si: 63-68%, C: 0.1%, S: 0.02%, P: 0.05%, Al: 2.5%, Mg: 0.4%, Cr: 0.4%)

ΦС75 (Si: 74-80%, C: 0.1%, S: 0.02%, P: 0.04%, Al: 3.0%, Mg: 0.4%, Cr: 0.3%)

Kremniy (Shelekhov) RUSAL. Ltd. For the needs of chemical and electrical industry enterprises No information

Na2O: 0.04%, MgO: 0.13%, Al2O3: 0.14, SiO2: 98.99, P2O5: 0.0060%, S: 0.0038%, K2O: 0.28%, CaO: 0.47%, TiO2 <0.001%, MnO: 0.015%, Fe2O3: 0.034%

On the basis of the table, it can be concluded that the chemical composition of MS is approximately similar for all the plants, but in some compositions, impurities of metals such as Na, Fe, Mg are dominant. It is known that impurities adversely influence the quality of the concrete mix. Consequently, the base-laying criterion for choosing a supplier is availability of a MS with a quantitative SiO2 content and a minimum amount of the content of impurities represented by foreign metals [9-11].

The technology of revealing the preferred properties acquired by concretes after the introduction of MS presupposes the account of the following performance characteristics (see Table 2) [12-16].

Table 2. Comparison of the exploitation characteristics.

| Indicator                                      | Standard composition | Composition using MS |
|-----------------------------------------------|----------------------|----------------------|
| Cement consumption, kg / m3                   | 470-530              | 200–450              |
| Compressive strength, MPa                     | 30-35                | 60–80                |
| Early strength when hardened under normal conditions, MPa (1 day) | 9-12                | 25–40                |
| Mobility (cone sedimentation, cm)             | 16-20                | 22–24                |
| Anticorrosion resistance                      | -                    | Reduction of water permeability down to 50 per cent, elevation of sulfate resistance by 100 per cent |
| Permeability for water and gases               | W2 — W12            | W12–W16              |
| Frost resistance                              | F50–F500             | F200–F600 (up to F1000 with special additives) |

The conclusion is obvious that the use of MS has a positive effect upon such properties of concrete as strength characteristics, frost-, wear-, sulfo- and chemical-resistance, permeability, resistance to abrasion, reduction in cement consumption, etc. [17-18].
Furthermore, different compositions of concrete have been analyzed with and without the use of MS, on the basis of which, the band of values for each index were chosen. Yu.M. Bazhenov’s monograph "Concrete Technology" gives the tentative composition of high-strength concrete, which has been taken as the basis [19]. There one can find an example of the composition of special high-strength concrete, which is shown in Table 3.

**Table 3. The tentative composition of high-strength concrete.**

| Components                             | Consumption of concrete, kg / m³ |
|----------------------------------------|---------------------------------|
| Portland cement                        | 400,0                           |
| MS                                     | 133,0                           |
| Quartz sand 0,25-1 мм                  | 141,0                           |
| Quartz sand 1-4 мм                     | 566,0                           |
| Larger filler                          | 1153,0                          |
| Naphthalene superplasticizer in the pro-powder form | 13,5                            |
| Water                                  | 100,0                           |

According to the results of our experiments, it has been confirmed that special attention should be paid to the naphthalene superplasticizer. This is a complex additive "Plasticizer S-3" ("S-3", hereinafter). According to the recommendations for the use of this complex additive, S-3 is intended for cast concrete mixtures and mortars with normal setting times [19-21].

Additive S-3 gives concrete a number of the following properties:
1. elevation of mobility from M1 to M5, and as a result – high workability,
2. high strength values as a reaction to mechanical impact,
3. lowered water consumption by 18–25%,
4. elevated water resistance, crack resistance, frost resistance (350 cycles);
5. reduction of cement consumption by 30-40%.

In connection with the conclusion obtained, we have performed the estimation of the final product cost. The market of construction materials has been analyzed, the prices of specific construction materials have been chosen and averaged, on the basis of which, an estimate of the final product cost per 1 m³ of the mixture was obtained. The data are given in Table 4.

**Table 4. The results of estimation of the final product cost per 1 m³ of the mixture.**

| Expenditures                     | Cost per ton of material | Material consumption (standard composition) | Material consumption (using MS) | Material cost (standard composition) | Material cost (using MS) |
|----------------------------------|--------------------------|---------------------------------------------|--------------------------------|--------------------------------------|-------------------------|
| Portland cement                  | 5000,0                   | 470,0                                       | 400,0                          | 2350,0                               | 2000,0                  |
| MS                               | 832,0                    | -                                           | -                              | 133,0                                | 110,6                   |
| Quartz sand 0,25-1 мм            | 2920,0                   | 760,0                                       | 141,0                          | 2219,2                               | 411,7                   |
| Quartz sand 1-4 мм               | 2120,0                   | -                                           | 566,0                          | -                                    | 1199,9                  |
| Larger filler                    | 720,0                    | 1000,0                                      | 1153,0                         | 720,0                                | 830,0                   |
| Naphthalene superplasticizer in the pro-powder form | 83,0                  | 13,5                                        | 13,5                           | 1,12                                 | 1,12                    |
| Water                            | 12,37                    | 176,0                                       | 100,0                          | 2,17                                 | 1,24                    |

Total:
Material cost (standard composition): 5293.5,5
Material cost (using MS): 4554,81
It can be concluded that addition of MS to the concrete formulation gives a positive effect expressed in the form of savings of cement, what leads to some reduction of the final product’s cost.

4. Conclusion
1. The market situation is currently characterized by wide availability of silicon manufacture waste products. Higher availability of MS allows one to expand the use of MS in the process of concrete manufacture. Application of MS obtained from the dust of gas purification in the process of silicon production shall increase in connection with (i) commissioning of dry gas purification at Russian Federation silicon plants and (ii) increase of inexpensive MS volumes at the market.
2. Realization of the potential created by the accessibility of the MS, necessitates some more advanced technologies for the production of concretes, including lightweight concretes, aerated concretes and foam concretes.
3. Since the dry waste in the form of MS has been started to obtain not very long ago, and their properties have not yet been fully studied, it is expedient to work in this direction, i.e. to conduct the in-depth study of the MS composition to understand possible variations of the properties and interactions with Portland cement.
4. The results obtained cannot be considered as final. There is the need to develop a material with the properties better than those achieved earlier. Therefore, the creation of concretes with improved operational and economic characteristics at the expense of additives in the form of MS obtained from wastes of silicon manufacture is an urgent problem allowing one to solve the following tasks: a) import substitution, b) cheaper end product, c) solution of environmental problems by using wastes of silicon manufacture in the form of microsilica.
5. Comparative evaluation of the MS modifying properties in the manufacture of high-strength heavy cement concrete provides for improvement of anti-corrosion and frost-resistant properties.
6. On the basis of data analysis for Russian Federation manufacturing enterprises, one can conclude that there are 5 enterprises on the territory of the Russian Federation from which one can purchase the MS needed.

References
[1] Application of microsilica in concrete plants. Electronic magazine “Construction” Retrieved from http://library.stroit.ru/articles/kremzem/index.html
[2] ASTM International Web site Retrieved from https://www.astm.org/cis/ru/index.html
[3] Holland T C 2005 Silica Fume User's Manual. Technical Report (Silica Fume Association) p 193
[4] Bergna H E 1994 The Colloid Chemistry of Silica (Am. Chem. Soc) p 718
[5] History & Manufacturing process. European Silica Fume Committee Retrieved from http://www.microsilicafume.eu/web/history%20and%20manufacturing%20process/1011306087/list1187970101/f1.html
[6] What is Silica Fume? - Silica Fume Association Retrieved from http://www.silicafume.org/general-silicafume.html
[7] Silica Fume In Concrete - The Silica Fume Association Retrieved from http://www.silicafume.org/general-concrete.html
[8] Bhanja S and Sengupta B 2003 Optimum silica fume content and its mode of action on concrete ACI Materials Journal pp 407–712
[9] Hooten R D 1993 Influence of silica fume replacement of cement on physical properties and resistance to Sulphate attack, Freezing and Thawing, and alkli silica reactivity ACI Material Journal pp 143–51
[10] Daniel Allen Mann 2014 The effects of utilizing silica fume in portland cement pervious concrete, Presented to the Faculty of the University of Missouri-Kansas City in partial fulfillment of the requirements for the degree (B.S. University of Missouri-Kansas City) p 98
[11] Hasan Biricika and Nihal Sarierb 2014 Comparative Study of the Characteristics of Nano
Silica- Silica Fume- and Fly Ash-Incorporated Cement Mortars’” Materials Research (Istanbul, Turkey) pp 570–582

[12] Zia P, Leming M L and Ahmad S H 1991 High Performance Concretes: A State-of-the-Art Report (Washington: Strategic Highway Research Program, National Research Council) Retrieved from https://www.fhwa.dot.gov/publications/research/infrastructure/structures/hpc/97030/chap1.cfm

[13] Powers T C 1958 Structure and Physical Properties of Hardened Portland Cement Paste Journal of the American Ceramic Society vol 41 1 pp 1–5

[14] Neville A M 1981 Properties of Concrete (London: Pitman Books Ltd) p 867

[15] Kumar Mehta P and Paulo J M 2014 Monteiro CONCRETE Microstructure, Properties and Materials (Canada) p 704

[16] Mamlouk Michael S and Zaniewski John P 2006 Materials for civil and construction engineers. Second edition (New Jersey) p 576

[17] Hewlett Peter C 2017 Lea’s Chemistry of Cement and Concrete (Oxford, UK) p 1000

[18] Hewlett Peter C 2003 Lea’s Chemistry of Cement and Concrete (Oxford, UK) p 1092

[19] Bazhenov Yu M 2003 Technologies of concrete (Moscow: Publishing House of the ASV) p 500

[20] Superplast. Additives for concrete Retrieved from http://superplast.su

[21] Superplast. Test laboratories for concrete Retrieved from http://www.himdobavki.ru