Classification of Quartzites by Gasification from a Mixture with Carbon Reducing Agents

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Abstract—Considerable time is required for industrial tests to assess the utility of quartz and quartzites in the production of silicon ferroalloys. A relatively simple method of classifying quartzite with respect to the production of silicon, ferroalloys, carborundum, and carborundum-bearing reducing agents has been devised on theoretical principles and introduced in practice. This method is based on measuring the degree of gasification of quartzites from a mixture with carbon reducing agents whose composition is calculated so as to ensure stoichiometry of the reaction $SiO_{2s} + C_s = SiO_v\uparrow + CO_g\uparrow$.

Keywords: metals, alloys, oxides, carbides, silicon, arc furnace, carbon-based materials

Silicon is the main component of silica ferroalloys (25−90% ferrosilicon, 35−50% ferrosilicochrome, 20−40% ferrosilicomanganese) and carborundum (97−99% SiC). Silicon is mainly derived from minerals containing 96−99% silica (SiO_2), such as quartz, quartzites, and sand. Quartzites are most commonly used in industry. They consist of densely cohesive quartz grains, with impurities of iron, calcium, aluminum, titanium, and other oxides. The table presents the chemical composition of industrial quartzites.

Industrial-grade silicon, ferrosilicon, and carborundum are obtained in direct-action electrofurnaces, by converting electrical energy to heat in the active resistances of the batch, arc, intermediate products, and final reduction products (alloy, slag).

The reduction of silicon is based on the following reactions:

—in the production of silicon and ferroalloys

$$SiO_2 + 2C = Si + 2CO, \quad (1)$$

$$SiO_2 + 2C + Fe = FeSi + 2CO, \quad (2)$$

—in the production of carborundum and carborundum-based reducing agents [1]

$$SiO_2 + 2C + Fe = FeSi + 2CO, \quad (3)$$

$$SiO_2 + (3 + n)C = SiC + nC + 2CO. \quad (4)$$

In all cases, the limiting stage is the dissociation of silica. In the atmosphere, the dissociation of SiO_2 is described by the equation

$$SiO_{2co} = SiO_g + 0.5O_{2g}, \quad (5)$$
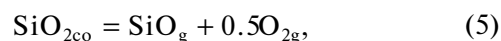
where the subscripts co and g denote the condensed and gas states, respectively.

Chemical composition and density of quartzites

| No.	Deposit	Notation	Content, %				Density, kg/dm³
			SiO₂	Al₂O₃	Fe₂O₃	CaO	
1	Pervouralsk quartzite (Karaulnaya mine)	PK	98.0	0.4	0.25	0.80	2.63
2	Bobrovsk quartzite	BK	97.0	1.7	0.80	0.30	2.64
3	Cheremshansk quartzite	ChK	98.5	0.4	0.20	0.30	2.68
4	Orlovsk quartzite (sand)	OK	97.0	1.0	0.40	0.33	1.34*
5	Khryustal'naya quartz	KKh	99.5	0.3	0.05	0.10	2.8

* Packing density.

ΔM, %
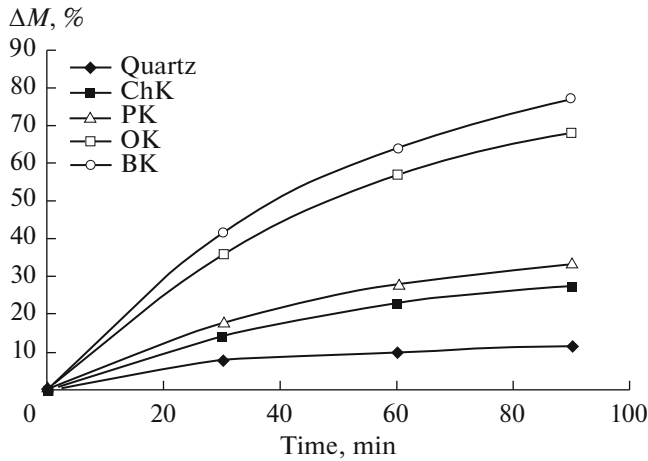
Decrease in mass of mixtures of quartzite with petroleum coke.

At atmospheric pressure, according to [2]

$$\Delta G_T^0 = 712\,685 - 225.09T. \qquad (6)$$

Hence, the equilibrium temperature in Eq. (6) is 2893°C. The formation of SiO in the presence of carbon may be described as follows

$$SiO_{2co} + C_{co} = SiO_g + CO_g. \qquad (7)$$
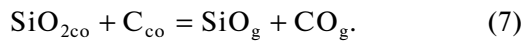
For this reaction

$$\Delta G_T^0 = 630\,828 - 335.61T. \qquad (8)$$

The equilibrium temperature when $\Delta G_T^0 = 0$ is 1633°C. With a motionless atmosphere, the cloud of SiO vapor above the solid SiO_2 slows dissociation. In the presence of carbon, the relatively heavy molecules of SiO vapor are displaced from the silica surface by a flux of relatively light gas (CO). In addition, the carbon from the reducing agent binds the molecules of SiO vapor in a chemically strong solid compound, carborundum

$$SiO_g + 2C_{co} = SiC_{co} + CO_g. \qquad (9)$$
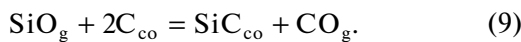
In this case

$$\Delta G_T^0 = 299\,551 - 166.03T. \qquad (10)$$

and hence the equilibrium temperature $t = 1531$°C. This creates favorable conditions for the gasification of silica according to Eq. (7).

In Eqs. (1)–(4), the products are formed in the sequence $SiO \rightarrow SiC \rightarrow Si$. In all stages, silicon monoxide SiO participates in the mass transfer. In particular, the silicon formation in the final stage is mainly the result of the reaction

$$SiO_g + SiC_{co} = 2Si_{co} + CO_g. \qquad (11)$$
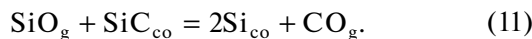
In this case

$$\Delta G_T^0 = 112\,147 - 68.55T. \qquad (12)$$

Hence, at equilibrium, $t = 1510$°C. Comparison of the equilibrium temperatures for Eqs. (7), (9), and (11) indicates that the temperature must be significantly higher than 1650°C in the limiting zone.

In electrofurnaces of shaft and Acheson type, much higher temperatures are attained, as is evident from the distribution of isotherms within the furnace's working chamber in the smelting of silicochrome and ferrosilicon [3].

It follows from practical experience in the production of silicon and ferroalloys on the basis of quartzites from various sources that, even with similar chemical composition, mechanical and thermal strength, melting point, and other properties, the economics of the process may be very different [4]. In particular, in the production of silicon, the replacement of quartzites by quartz, which has very low impurity content, significantly increases the power consumption (by 15−20%) and reduces the furnace productivity. In contrast to Pervouralsk quartzites (Karaulnaya mine), Bobrovsk quartzites depress furnace performance (by 5−8%) in the production of 45−65% ferrosilicon.

Direct industrial tests of new quartzites entail serious expenditures of money and time. Experiments in large laboratory furnaces (50−120 kV A) give encouraging results, which often fail to be confirmed in industrial tests. Laboratory research on the physicochemical properties of the materials does not permit clear conclusions.

According to thermodynamic analysis of the reduction of silicon, the best method of assessing natural quartzites is to measure the mass loss of a mixture of quartzites with carbon reducing agent, when the mixture composition is calculated in terms of the stoichiometry of the reaction in Eq. (7), where the molar ratio $C/SiO_2 = 1$. This method is also relatively simple.

Experiments on the gasification of quartzites are conducted in a Tamman resistance furnace and an induction furnace ($f = 2500$ Hz). The temperature is measured by a W−Re thermocouple. Crucibles with weighed portions of the reagents (particle size 0.1−1.0 mm) are placed in the working chamber of the furnaces. The volatile components (moisture from the quartzites, water, and volatiles from petroleum coke) are removed on heating to the specified reaction temperature (1680°C). The quantity of volatiles is taken into account in calculating the reaction masses for the pure silicon and carbon. The exposure time begins when the temperature reaches 1680°C. The furnace is switched off and the crucibles are cooled in the furnace to $t = 200$°C and then in air to room temperature. The residue is weighed, and the mass loss is calculated from the formula

$$\Delta M = \frac{M_{in} - M_{fin}}{M_{in}} \times 100\%. \qquad (13)$$

The exposure time is 30, 60, and 90 min.

In the figure, we show the decrease in mass for quartzites used in the smelting of 45−65% ferrosilicon

and silicon (PK and ChK quartzites) and in the industrial production of carborundum (OK quartzite). Note the large difference in the degree of gasification of these materials. The degree of gasification is assessed on the basis of the mass loss for OK quartzite (58%) and BK quartzite (64%).

The greater gasification of BK quartzite than of PK and ChK quartzite is probably the main reason for the poor economics of 45–75% ferrosilicon and silicon production in the trial runs [5–7]. In fact, the reduction of silicon corresponds to the total reaction in Eq. (1). The corresponding molar ratio $C/SiO_2 = 2$. The losses of silicon in monoxide form with the gas flux ($CO + CO_2$) when working with PK quartzite is 6–8% in the production of 45–65% ferrosilicon and 20% in silicon production. The SiO is captured at the surface formed by micropores and cracks in the pieces of carbon reducing agent [3]. When PK is replaced by BK quartzite, the vapor tension of SiO practically doubles. The loss of silicon with the gas phase increases correspondingly, and consequently the economics are impaired: the power costs increase and the silicon extraction is reduced.

In the production of 95% carborundum on the basis of Eq. (3), the molar ratio $C/SiO_2 = 3$. Hence, the total sorptional surface of the carbon in the batch increases by a factor of about 1.5. In the production of carborundum-based reducing agents, the molar ratio C/SiO_2 may be increased to 6, and the product will theoretically contain 53% SiC and 47% C. That reduces the loss of silicon as SiO by about half. Hence, quartzites characterized by greater gasification—in particular, OK and BK quartzites—should be used for carborundum production by the Acheson method and the production of carborundum-based reducing agents by a continuous process.

By measurement of the gasification in the specified mixtures, quartzites and quartz may be classified in terms of their suitability for the production of various silicon-bearing materials.

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