

Dissolution of Silica in Slag in Silicomanganese Production

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ABSTRACT

Carbothermal reduction of silica in silicomanganese production includes the dissolution of silica in slag and the reduction of silica from the slag. In industrial production of silicomanganese, with 17 – 20 wt% Si, the slag contains 38-44 wt% SiO₂, which is below the saturation level in equilibrium with quartz. On the other hand, the partitioning of silicon between metal and slag is generally close to equilibrium. This implies that the dissolution of quartz into the slag is the rate limiting step in the reduction process.

The dissolution rate and solubility of quartz in silicomanganese slags were studied in the temperature range of 1400 -1550 °C under argon. The dissolution rate of silica was measured using a rotating rod technique; the silica solubility was determined in static experiments using the drop-quench technique. The solubility of silica was also calculated using the Multiphase Equilibrium (MPE) thermodynamic software developed by CSIRO. The effects of additives (CaO, MnO, SiO₂ and Al₂O₃) on the quartz dissolution rate and solubility were also examined.

Under the experimental conditions employed the dissolution rate of quartz was controlled by mass transfer of silica in the slag. Silica diffusion coefficient in silicomanganese slag varied from 0.9×10^{-7} to 1.3×10^{-6} cm²/s, depending on temperature and slag composition. Activation energy for the diffusion of silica in the slag was found to be 367 kJ/mol. The addition of 10 wt% CaO decreased the activation energy to 115 kJ/mol, while the addition of 10 wt% Al₂O₃ increased the activation energy to 430 kJ/mol. The effect of slag composition on silica diffusivity is discussed in relation to the structure of molten slags.

The carbothermal reduction of silica from the mixture of manganese ore and quartz at 1600 °C in CO atmosphere was also studied. The experimental results are compared with equilibrium data calculated using FACTSage.

Introduction

SiMn alloy is produced in the temperature range of 1600-1650°C. Excavation of SiMn furnace [1] has revealed the presence of coke, liquid metal, slag and unreacted quartz in the reduction zone adjacent to the coke bed. Reduction of silica includes two processes; dissolution of quartz into the molten slag and reduction of dissolved silica to the metallic phase. Concentration of silica in SiMn slag is 38-44 wt% [1], which is much lower than the silica-saturation value [2]. This trend implies that the reduction of silica from SiMn slags is faster than the dissolution of quartz (cristobalite) into molten slag; therefore dissolution of silica into SiMn slag could be a rate limiting process in production of SiMn alloy.

Knowledge of the rate of dissolution of quartz into the slag is important for developing understanding of the reduction reactions. No data on the dissolution rate and diffusivity of silica in industrial SiMn slag were found in literature.

Dolan and Johnston [3] studied diffusion of Mn, Fe, Ca and Si in molten silicate slag (Al₂O₃, SiO₂, CaO) over the temperature range of 1400-1600°C using the semi-infinite capillary method. They found a relationship between “molecular structure” of melts and diffusivity. A decrease in the average size of the silicate anions resulted in increasing diffusivity of all species. Silicon exhibited the lowest effective diffusivity (10^{-6} cm²/s) among the examined species [3].

Liang et al. [4] used an isotope tracer method to measure self diffusion of calcium, aluminum, silicon and oxygen in molten CaO-Al₂O₃-SiO₂ at 1500 °C and 1 Gpa. According to their results, the self diffusion coefficients of species increased with the decreasing melt viscosity. They also found that self diffusion coefficient of silicon was the lowest ($1.8-39.2 \times 10^{-8}$ cm²/s) while calcium had the highest self diffusivity.

Keller and Schwerdtfeger [5] also used the capillary technique to measure the tracer diffusivity of Si in CaO-SiO₂ melts at 1600 °C. According to their results, the diffusivity of Si decreased with increasing silica content.

Mellberg and Lundstrom [6] studied the transfer of Si between a liquid Fe-Si alloy and molten CaO-Al₂O₃-SiO₂ slags with a small amount of CaF₂ at 1350°C and 1450°C using the electrochemical galvanostatic method. They found that the rate of transfer of Si was controlled exclusively by diffusion in the slag. According to their report, chemical diffusivity of silica in the slag increased from 10^{-7} cm²/s at 1350°C up to 10^{-6} at 1450°C.

The relationship between the structure of melts and their transport properties was examined by a number of investigators [7-11]. Mills [11] examined the relationships between structure of silicate slags and their viscosity, diffusivi-

ty and density; he demonstrated a good correlation between transport properties of melts and the depolymerisation parameter in such melts.

The present paper studied dissolution rate and diffusivity of silica in industrial SiMn slag at temperatures in the range of 1400 to 1550°C. Carbothermal reduction of silica from the manganese ore-quartz mixture was also examined at 1600 °C in CO atmosphere.

2. Experimental

2.1 Dissolution rate

The master slag supplied by Tasmanian Electro Metallurgical Company (TEMCO), was crushed and then kept in oven at 150 °C overnight to remove moisture. **Table 1** shows the chemical composition of the slag determined using XRF. The liquidus temperature of the master slag was estimated to be 1320°C.

Table 1. Chemical composition of industrial SiMn sla

Component	K ₂ O	MgO	MnO	CaO	Al ₂ O ₃	SiO ₂
Content, wt%	2.7	5.5	15.3	19.2	12.4	44.9

The dissolution experiments were conducted in a vertical tube furnace manufactured by the Ceramic Engineering Pty Ltd. The furnace consisted of three U-shaped MoSi₂ heating elements and an alumina tube (50 mm ID and 800 mm long). The temperature inside the furnace was monitored by a type R thermocouple located outside the furnace tube. Both ends of the furnace tube were sealed with water cooled fittings.

In rotating experiments, fused quartz rods (20 mm diameter and 200 mm long) in tolerances of ±1.5%, with a purity of >99% supplied by Technical Glass Products, Inc., USA were used. **Figure 1** shows a schematic of the experimental set-up. In each experiment, about 130 grams of crushed slag was contained in a Mo crucible (30 mm OD, 60 mm high) sitting on a platform which was placed on an alumina tube. The alumina tube had the provision for a type-R thermocouple.

During the process of furnace heat-up with rate of 300 °C/hour, the tip of the quartz rod was located in the center of hot zone while the Mo crucible containing slag was positioned about 10 mm below the quartz rod. After reaching the target temperature, the slag was allowed to homogenize for 2 hours. Argon with flow rate of 0.3 L/min was passing through the system during experiment.

The Mo crucible was then raised manually to immerse 25-40 mm of quartz rod in molten slag and then quartz rod started rotating. For sampling at different time intervals, Mo crucible was lowered down to the initial position and slag was sampled using a cold Mo strip (2 mm wide). The Mo strip was dipped into molten slag from top of the furnace, then quickly removed and rapidly quenched in cold water. The slag samples were dried in an oven overnight and crushed for XRF analysis.

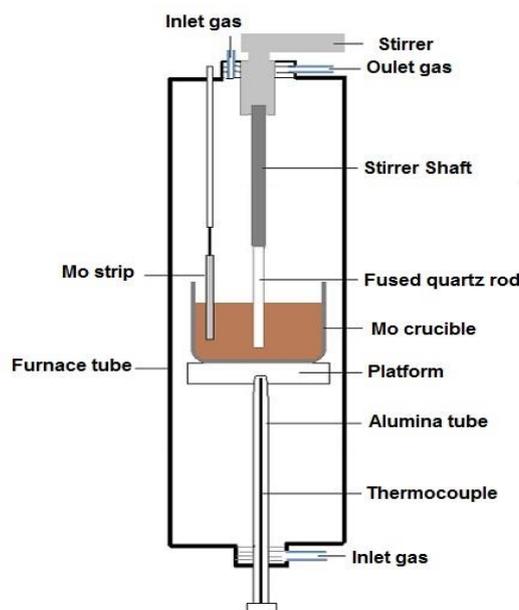


Figure 1. Schematic of rotation experiment set up

The solubility of silica in SiMn slag was measured by reaction between quartz crucible and slag under static condition. In each experiment, about 1 gram of slag was contained in the crucible (10 mm ID and 30 mm high) which was attached to a long alumina tube using Pt/Rh wire. Alumina tube with silica crucible was introduced to the furnace from top. Silica crucible was placed in the hot zone of the furnace and heated to the target temperature with rate of 300°C/hr. After reaching the experimental target temperature, crucible was kept in the hot zone for required reaction time.

In order to quench the sample, alumina tube was lowered down; the crucible was unattached from alumina tube to drop in a bucket of cold water placed under the furnace. The silica crucible with its content was cut and mounted in resin followed by polishing for SEM-EDS analysis.

2.2 Reduction experiments

The quartz rod used for dissolution rate experiment was grinded down to the size of 1-2 mm and then mixed with crushed manganese ore (106-200 μm) supplied by GEMCO (Groote Eylandt Mining Company). XRF analysis of the ore is given in **Table 2**. Carbothermal reduction of manganese ore-quartz mixtures with ratios of 2 to 1 and 1 to 1 with 30 wt% excess carbon was studied at 1600°C. The experimental set-up for the carbothermal reduction was presented elsewhere [12].

Table 2. Chemical composition of manganese ore

Component	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	MnO ₂	K ₂ O	Na ₂ O	MgO
Content, wt%	4.2	11.1	5.5	75.0	2.2	0.5	0.2

3 Experimental results

3.1 Static experiments

The quenched samples from static experiment were analysed using SEM/EDS analysis. **Table 3** represents the average EDS data of the bulk slag reacted with silica for 360 minutes at temperatures of 1400, 1450 and 1500°C.

Table 3: EDS analysis of the bulk slag in static experiments

Slag temperature °C	Slag composition (wt%)				
	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO
1400°C	64.0	8.6	13.3	3.9	9.7
1450°C	64.8	8.1	12.4	3.6	9.1
1500°C	68.8	7.4	11.2	3.3	8.3

Thermodynamic modeling was carried out using CSIRO's Multi-Phase Equilibrium (MPE) model [13] to calculate solubility of SiO₂ in the slag of given composition (Table 1). Experimental results were in a very good agreement with MPE data which shows that in static experiments slag was close to equilibrium with quartz.

3.2 Rotating rod experiments

Effect of the rotation speed on the dissolution rate of quartz in the industrial SiMn slag was studied at the temperature of 1500°C in the range of 40 to 100 revolutions per minute (RPM). The rate of silica dissolution was calculated using the following equation [14]:

$$rate = \frac{slope * W}{100 * A * 60} \quad (1)$$

Where *slope* (wt%/min) is the slope of SiO₂ concentration curve versus reaction time, which was obtained by fitting a straight line through experimental concentration data. *W* (g) is the mass of slag and *A* (cm²) is the total area of silica rod in contact with molten slag. Silica rod used in this experiment was considered as consisting of a disk at the bottom and cylinder at the wall. The cylinder height was assumed to be the depth of immersion of the rod into molten slag. Consequently total area was assumed to be the area of disk and cylinder in contact with slag.

3.3 Reduction experiments

Weight losses measured after 60 minutes carbothermal reduction of manganese ore-quartz mixtures in ratios of 2 to 1 and 1 to 1 were 38.9 % and 24.8%, respectively.

Figures 2 and 3 show XRD spectra of reduced manganese ore-quartz mixtures when they were mixed in ratio of 2 to 1 and 1 to 1, respectively. In reduced manganese ore-quartz mixture with ratio of 2 to 1, no cristobalite was detected by the XRD analysis. However XRD spectra of the reduced mixture with ratio of 1 to 1 included cristobalite peaks.

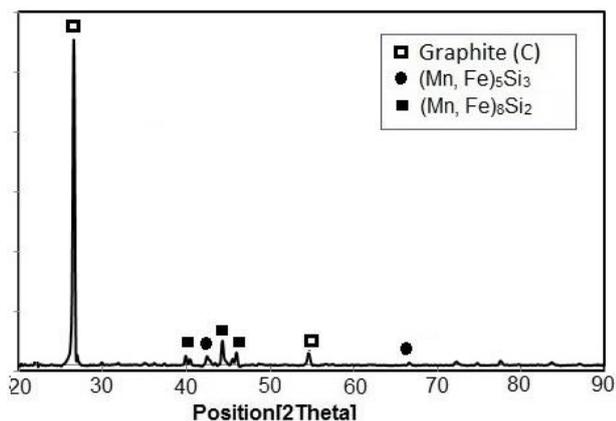


Figure 2. XRD pattern of the manganese ore-quartz mixture with ratio of 2 to 1 reduced at 1600°C for 60 minutes

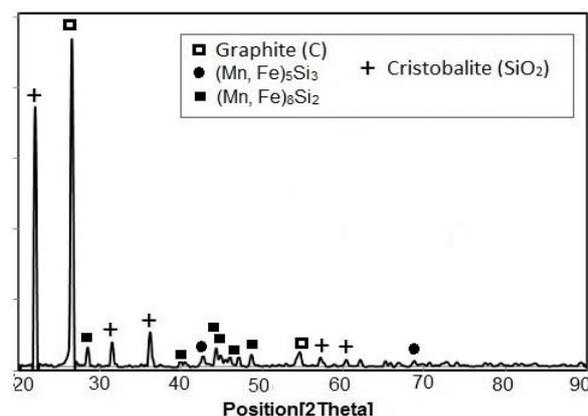


Figure 3. XRD pattern of the manganese ore-quartz mixture with ratio of 1 to 1 reduced at 1600°C for 60 minutes

The XRD analysis of the reduced samples identified manganese-iron silicides, which were formed during process of cooling and solidification. EPMA results showed that the alloy phase formed in the 60-min reduction of manganese ore-quartz mixture with ratio of 2 to 1 contained 20.6 wt% Si, 74 wt% Mn and 6.4 wt% Fe; in the reduction of the manganese ore-quartz mixture with ratio of 1 to 1, the alloy contained 18.8 wt% Si, 74.1wt% Mn and 6.5 wt% Fe.

When manganese ore and quartz were mixed at a ratio of 1 to 1, different slag phases were formed. Results of EPMA of the slag phases formed in carbothermal reduction of manganese ore-quartz mixture with ratio of 1:1 for 60 minutes reaction times are shown in **Table 4**. In average, silica content of the slag phase formed during carbothermal reduction of Mn ore-quartz mixture with ratio of 1:1 was higher than in the reduction of the mixture with 2:1 ratio. This confirms that in the case of manganese ore-quartz mixture at a ratio of 1:1, silica concentration in slag reached the saturation level, while in the reduction of the mixture with 2:1 ratio, all quartz was dissolved in the slag; no cristobalite was detected by SEM/EDS and XRD analyses.

Table 4: EPMA analysis of slag phase in the manganese ore-quartz mixture with ratio 1 to 1 reduced at 1600°C (wt%) for 60 minutes.

A: Slag1

Al	Si	O	Mn	K
1.2	31.0	43.9	23.2	0.7
1.7	31.9	45.6	19.9	0.9
1.4	26.7	54.2	17.0	0.6

B: Slag 2

Al	Si	O	Mn	K
2.6	36.2	49.3	9.8	2.0
2.5	35.7	49.1	10.8	1.9
2.2	35.9	48.8	11.1	1.9
2.1	35.6	48.7	11.8	1.7
2.0	35.2	48.4	12.6	1.7
1.3	35.5	49.1	13.0	1.3
1.0	35.1	51.5	11.4	0.9
1.1	36.1	49.2	12.6	0.9

C: Slag3

Al	Si	O	Mn	K
8.3	30.8	49.9	7.0	3.9
8.2	30.8	50.3	6.7	3.9
5.1	36.2	51.5	4.0	3.2
4.3	36.6	52.0	4.0	3.1
4.0	36.7	51.3	4.8	3.2
3.6	36.9	51.4	5.0	3.1

SEM images of reduced samples are presented in **Figures 4 and 5**. SiC was observed in the reduced samples, although it was not detectable by the XRD analysis.

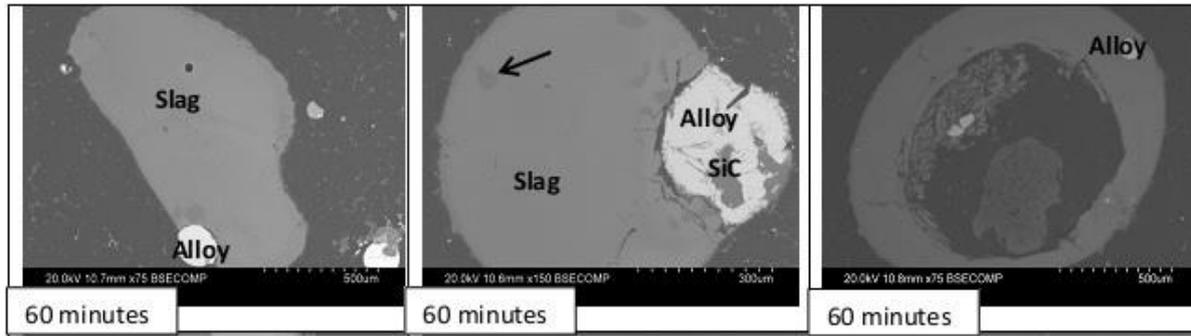


Figure 4: SEM images of manganese ore-quartz mixtures (ratio 2 to 1) reduced in CO at 1600°C for reaction time of 60 minutes.

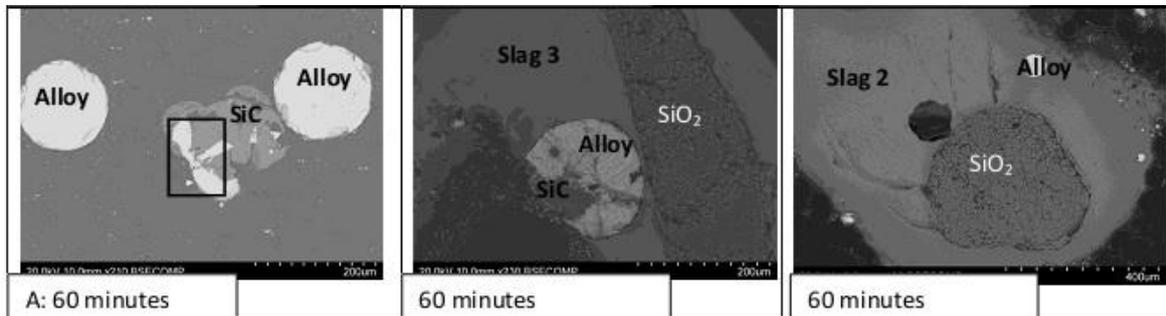


Figure 5: SEM images of manganese ore-quartz mixtures (ratio 1 to 1) reduced in CO at 1600°C for 60 minutes.

4 Discussion

4.1 Silica diffusivity in the SiMn slag

The chemical diffusivity of silica in slags was determined from experimental data on the rate of quartz dissolution obtained using the rotating rod technique. Mass transfer from the rotating silica rod consisted of two fluxes from disk side and cylindrical side of the rod. Mass transfer from the disk and cylinder sides of the silica rod can be described by Levich-Cochran [15] and Kosaka et al. [16] correlations, respectively. The following equation for the total mass transfer coefficient (k_{total} (cm/s)) was derived based on the mass flux from disk and cylinder sides of the silica rod:

$$k_{total} = \frac{r}{r + 2h} 0.621 D^{2/3} \omega^{1/2} \left(\frac{\rho}{\mu}\right)^{1/6} + \frac{2h}{r + 2h} 0.055 D^{2/3} r^{1/2} \omega^{3/4} \left(\frac{\rho}{\mu}\right)^{5/12} \quad (2)$$

where ω (rad/s) is angular velocity of the disk ($V = \omega.r$), r is the radius of the silica rod and h is the length of the rod immersed in the slag; ρ , μ and D are slag density, slag viscosity and diffusivity.

The total mass transfer coefficient can be calculated using the experimental rate of dissolution, according to the following equation:

$$k_{total} = \frac{rate}{(C_s - C_b) \cdot \rho_{slag}} \quad (3)$$

where C_s and C_b are concentrations of SiO₂ (wt%) at silica-slag interface and in bulk slag, respectively. Slag density ρ_{slag} was estimated by a model proposed by Mills and Keene [17]. Chemical diffusivity was calculated using equations (2) and (3).

According to equation (2) total mass transfer coefficient is proportional to the rotation speed with power of 0.5 for disk and 0.75 for cylinder. In the case in which the dissolution is controlled by mass transfer in the liquid slag, it is expected that the dissolution rate of a disk increases linearly with the square root of rotation speed [18] and, when a rotating cylinder is used, the increase in the rate is proportional to the rotation speed in the power of 3/4 [19]. **Figure 6**

shows a linear dependence of dissolution rate of silica in molten SiMn slag on the 0.5th and 0.75th power of rotation speed at 1500°C, respectively. This implies that under experimental conditions in this work, mass transfer in the liquid phase controls the dissolution rate of silica.

Dissolution rate and diffusivity were measured in the temperature range of 1400-1550 °C with a rotation speed of 60 RPM. At 1400°C, dissolution rate and diffusivity were found to be 3.2×10^{-6} (g.cm⁻².s⁻¹) and 1.1×10^{-7} (cm²/s) respectively. With increasing temperature to 1550°C, the dissolution rate and diffusivity increased to 2.5×10^{-5} (g.cm⁻².s⁻¹) and 1.2×10^{-6} (cm²/s). The uncertainty in estimation of the diffusivity was about ±36 % which is deduced from errors/uncertainties in calculation of the slope of SiO₂ concentration data, weight of molten slag, contact area between the quartz rod and slag and dissolution rate data.

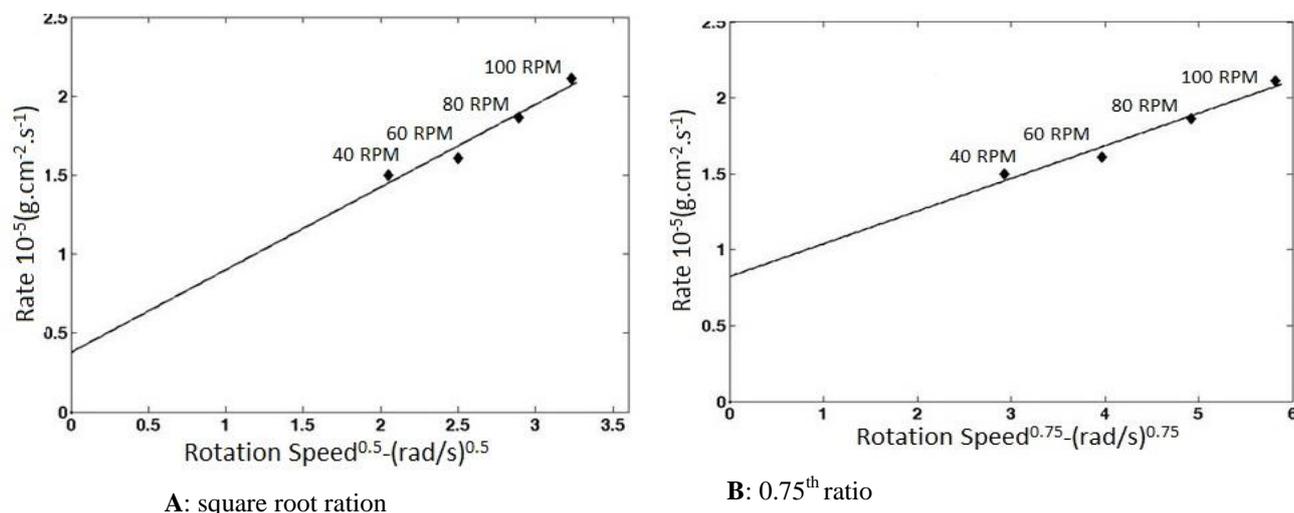


Figure 6. Dependence of the dissolution rate of silica in SiMn slag on the rotation speed at 1500°C; A: in the power of 0.5, and B: in the power of 0.75,

To investigate and quantify the effects of additives on the rate of quartz dissolution and diffusivity of SiO₂ in industrial slag, SiO₂, Al₂O₃, CaO or MnO were added to the master slag in the amount of 10 wt%. The deduced results obtained over the temperature range of 1450-1550°C are listed in **Table 7**. The viscosity of these slags was predicted by the MPE software package. The results summarized in **Table 7** show the increase in the silica dissolution rate and diffusivity with increasing temperature, and additions of MnO and CaO. Addition of Al₂O₃ and SiO₂ decreased the dissolution rate and diffusivity.

Table 7: Measured dissolution rate and diffusivity of SiO₂ in the slag with 10 wt% addition of SiO₂, Al₂O₃, CaO and MnO

Slag	Initial Slag Composition wt%	Temperature °C	Dissolution rate (gr.cm ⁻² .s ⁻¹)	Diffusivity (cm ² /s)
Master slag	SiO ₂ (40.8), Al ₂ O ₃ (11.3), MnO(13.9), CaO(17.4), MgO(5), K ₂ O(2.4)	1450°C	1.1×10^{-5}	8.2×10^{-7}
		1500°C	1.6×10^{-5}	8.4×10^{-7}
		1550°C	2.5×10^{-5}	1.2×10^{-6}
Master slag+10% Al ₂ O ₃	SiO ₂ (40.8), Al ₂ O ₃ (20.4), MnO(13.9), CaO(17.4), MgO(5), K ₂ O(2.4)	1450°C	4.4×10^{-6}	9.4×10^{-8}
		1500°C	8.1×10^{-6}	1.9×10^{-7}
		1550°C	1.8×10^{-5}	4.9×10^{-7}
Master slag+10% CaO	SiO ₂ (40.8), Al ₂ O ₃ (11.3), MnO(13.9), CaO(26.5), MgO(5), K ₂ O(2.4)	1450°C	2.2×10^{-5}	8.4×10^{-7}
		1500°C	2.9×10^{-5}	1.1×10^{-6}
		1550°C	4.3×10^{-5}	1.3×10^{-6}
Master slag+10% SiO ₂	SiO ₂ (49.9), Al ₂ O ₃ (11.3), MnO(13.9), CaO(17.4), MgO(5), K ₂ O(2.4)	1450°C	2.7×10^{-6}	1.5×10^{-7}
		1500°C	5.9×10^{-6}	3.9×10^{-7}
		1550°C	1.2×10^{-5}	6.4×10^{-7}
Master slag+10% MnO	SiO ₂ (40.8), Al ₂ O ₃ (11.3), MnO(13.9), CaO(17.4), MgO(14.3), K ₂ O(2.4)	1450°C	1.8×10^{-5}	7.3×10^{-7}
		1500°C	2.4×10^{-5}	9.5×10^{-7}
		1550°C	3.3×10^{-5}	1.3×10^{-6}

Feichtinger et al. [20] measured diffusivity of silica in slag containing 54.6 wt% SiO₂, 34.1 wt% CaO, and 10.6 wt% Al₂O₃; diffusivity of silica was found to have a magnitude of 10⁻⁷ cm²/s, which is in a good agreement with

the experimental data of the present work for SiO₂ dissolution in the industrial slag with addition of 10 wt% CaO at 1450 °C.

The observed effects of additives such as CaO on the diffusivity of SiO₂ at 1450 °C in the SiMn industrial slag are in a good accord with published data [21] on self diffusivity of Si in slag containing 21 wt% Al₂O₃- 39% CaO-40% SiO₂ at 1430°C.

Silicate melts have a complex structure. With increasing silica content of the melt, the SiO₄⁻⁴ tetrahedra anions are linked together to form large-size silicate anions and gradually develop into network structure. In this structure, nearly all oxygen atoms act as bridges between two silicon atoms [22].

Addition of basic oxides (CaO, MnO and others) to silicate melts results in break down of silicate network and formation of non-bridging oxygen ions. Such oxygen ions are bonded to both network modifying metal cations (Ca²⁺, Mn²⁺) and tetrahedrally coordinated cations (Si⁴⁺) in the silicate network [21].

Additions of SiO₂ and Al₂O₃ to the slag slowed down the dissolution rates and diffusion of SiO₂ in the slag. Addition of SiO₂ to the slag decreased the number of non-bridging oxygen while the number of bridging oxygen increased. Expansion of a network of SiO₄⁻⁴ tetrahedra slowed the movement of anions leading to a slower diffusion of SiO₂ in slag. Since the original master slag contains high amount of silica, the number of non-bridging oxygen is so limited.

The effect of Al₂O₃ on physical and transport properties of the slag at a given silica content depends upon the ratio of alumina to metal cations such as Ca²⁺, Mn²⁺, K⁺ (R=alumina/metal oxide) [23-27]. In the slag studied in the present work, the number of charge compensators is higher than the number of AlO₄⁵⁻ tetrahedra (R<1). With addition of 10 wt% Al₂O₃ to the industrial slag, alumina acts as a network former causing increase of the slag viscosity and slowing silica diffusion.

Effect of temperature on the diffusion of silica can be described by the Arrhenius equation [14]:

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \tag{11}$$

where D_0 is constant; Q is activation energy for diffusion (J/mol) and R is the universal gas constant (=8.3144 J.mole⁻¹.K⁻¹). The chemical diffusivity of silica in the slags versus reciprocal of temperature is shown in **Figure 7**.

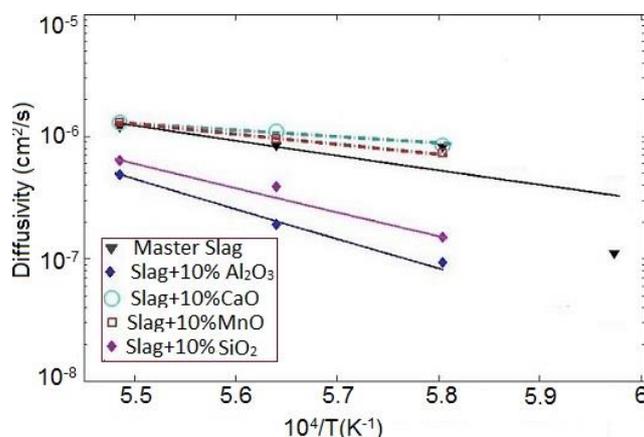


Figure 7. Variation of the diffusivity of silica in the slags with reciprocal of temperature

The activation energy for silica diffusion in the SiMn slag (367 kJ/mol) decreased considerably with the addition of CaO (115 kJ/mol) and MnO (132 kJ/mol). However the addition of Al₂O₃ and SiO₂ had the opposite effect. With the addition of 10wt% Al₂O₃ to the SiMn slag, the activation energy increased to 430 kJ/mol.

4.3 Reduction of the manganese ore-quartz mixtures

Chemical composition of equilibrium phases formed in carbothermal reduction of manganese ore-quartz mixtures at 1600°C in CO atmosphere were calculated using FACTSage software Version 6.2. **Tables 5** and **6** show the equilibrium chemical composition of the slag in the reduction of manganese ore-quartz mixtures with ratios of 2 to 1 and 1 to 1, respectively.

Stoichiometric amounts of graphite for reduction of iron, manganese and silicon oxides to carbides (Fe.Mn)₇C₃ and SiC in 100 gr of the mixture of manganese ore-quartz in ratios of 2 to 1 and 1 to 1, were 46 and 41 g, respectively. The calculated equilibrium chemical compositions by FACTSage are in a good accord with EPMA results.

The results predicted by FACTSage for carbothermal reduction of the ore-quartz mixtures show the effect of the amount of graphite added to the mixture on equilibrium phases and chemical composition of phases.

Calculation of equilibrium phases confirmed that in the reduction of the ore-quartz mixture with ratio 2:1, all quartz was dissolved into the slag phase before the reduction started; neither quartz nor cristobalite were observed in the reduction experiments with this mixture. When the ore-quartz ratio was 1:1, cristobalite was in equilibrium with the slag phase; experiments showed that the silica concentration in the slag was close to saturation.

In the presence of excess carbon, calculations showed that all silica was reduced to the metallic phase and SiC. However, in experiments with the ore-quartz mixture with 1 to1 ratio, cristobalite was observed even after 60-min reduction; equilibrium was not reached.

Concentration of silica in the slag from the laboratory reduction experiments was close to the saturation level. However, in industrial production of SiMn, silica concentration in the slag was well below the saturation. The difference between the results of the reduction experiments and industrial data can be attributed to the difference in the quartz-slag contact area. In the laboratory experiments, slag and quartz (1-2 mm particles) were well-mixed and had a high contact area. In the excavation of the silicomanganese furnace, observed quartz lumps (up to 50 mm) had a limited contact with the slag phase. Dissolution of quartz in the rotating rod experiments, controlled by the mass transfer of silica in the slag, was also slow. In these experiments, the surface area of the quartz rod immersed into the molten slag was relatively small but the molten slag was well agitated and mixed by the rotating rod. In the static experiments in which dissolution of quartz crucible into the molten slag was examined, slag in the vicinity of the crucible was saturated with silica within relatively short reaction period, however the bulk slag was not at saturation after 30, 60 or 90 minutes of reaction; it reached the saturation level after 180 minutes.

Table 5: Equilibrium chemical composition of liquid slag (wt pct) in the process of reduction of manganese ore (98.7 g, **Table 2**) -quartz (50 g) mixture at 1600 °C calculated using FACTSage

Amount of graphite added to the mixture, g	SiO ₂ / a _{SiO₂}	MnO/ a _{MnO}	Al ₂ O ₃	FeO	K ₂ O	Na ₂ O	MgO
0	45.5/0.552	45.5/0.100	4.09	2.81	1.59	0.368	0.149
25	59.4/0.855	30.2/0.0471	7.71	1.72x10 ⁻³	1.84	0.560	0.278
50	40.6/0.377	26.2/0.0222	28.7	6.76x10 ⁻⁴	0.418	2.18	1.84
75	-	-	-	-	-	-	-

Table 6: Equilibrium chemical composition of liquid slag (wt pct) in the process of reduction of manganese ore (98.7 g, **Table 2**) -quartz (100 g) mixture at 1600 °C calculated using FACTSage

Amount of graphite added to the mixture, g	SiO ₂ / a _{SiO₂}	MnO/ a _{MnO}	Al ₂ O ₃	FeO	K ₂ O	Na ₂ O	MgO
0	57.9/0.963	35.1/0.0569	3.16	2.17	1.25	0.286	0.115
25	66.7/0.963	24.0/0.0431	6.48	1.6x10 ⁻³	2.08	0.512	0.234
50	78.7/0.886	8.11/0.0255	8.76	4.4x10 ⁻⁶	3.33	0.756	0.304
75	45.1/0.495	28.2/0.0229	24.0	9.8x10 ⁻⁴	0.468	1.41	0.910

5 Conclusions

Dissolution rate of fused silica rod in the SiO₂-CaO-MnO-Al₂O₃-MgO-K₂O slags was measured at temperatures between 1400 and 1550 °C under argon using the rotating rod method. The dissolution rate increased with addition of CaO and MnO to silicomanganese slag, while addition of SiO₂ and Al₂O₃ to the slag resulted in slower dissolution rate.

The solubility of silica in silicomanganese slag was also studied through a series of static experiments as well as through thermodynamic modeling using the MPE model. The experimental data were found to be in a good agreement with calculated values.

Experimental data on quartz dissolution rate and silica solubility were used to calculate silica diffusivity in silicomanganese slag with addition of 10 wt% of SiO₂, Al₂O₃, CaO and MnO. The diffusivity coefficient varied from 0.9x10⁻⁷ to 1.3x10⁻⁶ cm²/s, depending on temperature and slag composition. Activation energy for the diffusion of silica in silicomanganese slag was found equal to 367kJ/mole; it decreased significantly to 115kJ/mole with the addition of 10 wt% CaO. Al₂O₃ had an opposite effect increasing the activation energy to 430kJ/mole.

Carbothermal reduction of manganese ore and quartz mixtures in the ratios of 2 to1 and 1 to1 were conducted in CO gas atmosphere at temperature of 1600°C. Reduced manganese ore-quartz mixture with ratio of 1:1 contained cristobalite and iron-manganese silicides which were formed in cooling process. SiC was also detected in SEM/EDS analysis of reduced samples. No cristobalite was observed in reduced manganese ore-quartz mixture with ratio of 2 to 1. Silica content in the slag in reduction of the ore-quartz mixture with 1:1 ratio was close to the saturation level.

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References

- [1] Olsen, S., Tangstad, M. and Lindstad, T. Production of Manganese Ferroalloys, Tapir, Trondheim, 2007.
- [2] Ostrovski. O and Swinbourne. D. *Steel Res. Int.*, 2013, 84 (7), pp 680-686.
- [3] Dolan. M. D and Johnstone. R.F. *Metall. Mater. Trans. B.*, 2004, 35 B, pp675-684.
- [4] Liang. Y; Richter. F. M; Davis. A.M and Watson. E.B.. *Geochim. Cosmochin. Ac.*, 1996, 60(22), pp 4353-4367.
- [5] Keller. H and Schwerdtfeger. K. *Met. Trans. B.*,1979, 10B, pp. 551-554.
- [6] Mellberg, P. O and Lundstrom, P. A. *Transactions ISIJ*,1981, 21, pp. 592-595.
- [7] Bockris. J. O'M; Mackenzie. J. D and Kitchener. J. A. *Trans. Farad. Soc.*, 1954, 51, pp. 1734-1747.
- [8] Bockris. J. O'M and Reddy. A. K. N. *Modern Electrochemistry*, Plenum Press, New York, 1970.
- [9] Zhang. G.H; Chou. K. C; Xue. Q. G and Milla. K. *Metall. Mater. Trans. B.*, 2012, 43 B, pp. 64-72.
- [10] Zhang. G.H; Chou and Milla. K. *ISIJ International*, 2012, 52 (3), pp. 355-362.
- [11] Mills. K., *ISIJ International*, 1993, 33(1), 148-155.
- [12] Maroufi. S; Ciezki. G; Tangstad. M; Jahanshahi. S and Ostrovski.O. *INFACON XIII*, Almaty, Kazakhstan, June 9-13, 2013.
- [13] Zhang, L., Jahanshahi, S., Sun, S., Chen, C., Bourke, B., Wright, S., and Somerville, M. A. *JOM*, 2002, 54 (11), pp. 51-56.
- [14] Amini. S.H; Brungs. M. P; Jahanshahi. S and Ostrovski. O. *Metall. Mater. Trans. B.*, 2006, 37B, pp. 773-780.
- [15] Cochran. W. L. *Proceedings of the Cambridge Philosophical Society*,1934, 30, pp. 365-374.
- [16] Kosaka. M and Minowa. S. *Tetsu.To. Hagan* 1966, 52(12), pp. 22-36.
- [17] Mills. K. C and Keene, B., *J. International Materials reviews*, 1987, 32 (1-2), 1-120.
- [18] Levich. V. G. *Physiochemical Hydrodynamics*, Prentice-Hall, New York, NY, 1962, p. 69.
- [19] Eisenberg. C. W and Tobias. W. *Chemical Engineering Progress Symp. Series*, 1995, 51, Mills. K., *ISIJ International*, 1993, 33(1), 148-155.
- [20] Feichitinger. S; Michelic. S. K; Kang. Y and Bernhard, C., *J. Am. Ceram. Soc.*, 2014, 97(1), pp316-325.
- [21] *Slag Atlas*, 2nd Edition 03, Edited by Verein Deutscher Eisenhüttenleute, 541-556, 1995.
- [22] Mysen, B. O. *Structure and Properties of Silicate Melts*. Elsevier, Amsterdam. 1988.
- [23] Urbain. G; Cambier. F; Deletter. M; Anseau. M.R. *Brit., Ceram. Trans J*, 1981, 80, 139-141.
- [24] Zhang. L and Jahanshahi. S. *Scand. J. Metall.*, 2001, 30, 364-369.
- [25] Park. J. H; Min. D. J and Song. H. S. *Metall. Mater. Trans. B.*, 2004, 35 B, 269-275.
- [26] Zhang. L; Sun. S and Jahanshahi. S. *Journal of Phase Equilibria and Diffusion*, 2007, 28 (1), 121-129.
- [27] Zhang. L; Sun, S and Jahanshahi. S., *J. non-Cryst Solids*, 2001, pp. 24-29.