Mathematical model of silicon smelting process basing on pelletized charge from technogenic raw materials

N V Nemchinova, A A Tyutrin, V M Salov

Irkutsk National Research Technical University, 83, Lermontov St., Irkutsk, 664074, Russia

E-mail: ninavn@yandex.ru

Abstract. The silicon production process in the electric arc reduction furnaces (EAF) is studied using pelletized charge as an additive to the standard on the basis of the generated mathematical model. The results obtained due to the model will contribute to the analysis of the charge components behavior during melting with the achievement of optimum final parameters of the silicon production process. The authors proposed using technogenic waste as a raw material for the silicon production in a pelletized form using liquid glass and aluminum production dust from the electrostatic precipitators as a binder. The method of mathematical modeling with the help of the ‘Selector’ software package was used as a basis for the theoretical study. A model was simulated with the imitation of four furnace temperature zones and a crystalline silicon phase (25 °C). The main advantage of the created model is the ability to analyze the behavior of all burden materials (including pelletized charge) in the carbothermic process. The behavior analysis is based on the thermodynamic probability data of the burden materials interactions in the carbothermic process. The model accounts for 17 elements entering the furnace with raw materials, electrodes and air. The silicon melt, obtained by the modeling, contained 91.73 % wt. of the target product. The simulation results showed that in the use of the proposed combined charge, the recovery of silicon reached 69.248 %, which is in good agreement with practical data. The results of the crystalline silicon chemical composition modeling are compared with the real silicon samples of chemical analysis data, which showed the results of convergence. The efficiency of the mathematical modeling methods in the studying of the carbothermal silicon obtaining process with complex interphase transformations and the formation of numerous intermediate compounds using a pelletized charge as an additive to the traditional one is shown.

1. Introduction

The production of various metals and alloys is accompanied by the formation of a significant amount of technogenic waste, causing considerable consequences for the environment. This problem requires utilization of the technogenic waste and, if possible, its reuse, for example, as a raw additive to the main charge [1].
At the largest enterprise in Russia, ‘Kremniy’ JSC (Shelekhov, Irkutsk region), the united company RUSAL, the production of silicon is carried out continuously in three-phase three-electrode open rotary furnaces with the capacity of 16.5 and 25 MW*A, working on alternating current, with the temperature of the working zone of about 2200 °C [2, 3].

EAFs are equipped with coal electrodes produced by the Novosibirsk electrode plant of the ‘Energoprom’ group of the companies. The main limiting impurities in the quartzite of the Cheremshansky deposit, which is used as the raw material, are iron, aluminum and calcium oxides. At the enterprise, a combination of carbon-containing materials in various ratios is used as reducing agents. It allows saving charcoal, expensive but the most reactive material, reducing the flow of impurity elements into the process by using a low-ash petroleum coke, conducting the smelting process in the optimal mode using coal from the Kazakhstan and Colombian industries. When silicon is melted from quartz raw materials, cyclones and wet gas purification mud, refinery slags and pot-scraps are formed in the EAF. However, these products are promising raw materials since they contain valuable components that can be partially or completely returned to the technology cycle.

The main target of the current research is the application of mathematical modeling to the process of silicon recovery in the EAF using a pelletized charge, consisting of fine-grained technogenic raw materials of silicon and aluminum industries, as an additive to a traditional (lumped) charge.

2. Creation of mathematical model

The authors developed a charge lumping technique for the charge [4], consisting of cyclone dust of the gas purification system being the main silica-containing raw material; fine-scale silicon screening from the ‘Kremniy’ JSC; petroleum coke as a carbonaceous reducing agent; dust of electrostatic precipitators produced in the aluminum production (PJSC ‘RUSAL Bratsk’, Shelekhov branch) and liquid glass as a binder (Figure 1).

![Figure 1](image_url)  
**Figure 1.** Technogenic raw materials: a – pelletized charge; b – dust from the silicon production cyclones (SE image, 8500x magnification).

These pelletized compositions can be added to the standard charge in crystalline silicon smelting in the EAF [4]. The mathematical modeling with the aid of the ‘Selector’ software package was used to analyze the behavior of the new charge components during the smelting process. The model is based on the Gibbs energy minimization and widely used for modeling the high-temperature metallurgical processes [5 – 8]. One of the main advantages of this soft is the ability to model reservoirs dynamics (for example, in the following system: ‘lumped charge – pelletized charge – electrodes – air – melt – slag – gases – crystallized silicon’), which allows the most complete and accurate reproduction of the basic laws governing technological processes.

The mathematical model is based on the algorithm of the carbothermic process of the metal silicon production with the determination of the number of the reservoir, each of which corresponds to a certain temperature zone (zone of the main chemical reactions of the silicon production) [9, 10].
This algorithm is represented below:

**Determination of the temperature zones of the silicon production reactions in the EAF and the number of reservoirs**

**The choice of the simulated system components with the consideration of the chemical analysis data on the charge components**

**Data preparation and charge rate calculation for the input to the model**

**Scheme development for the reservoirs interaction by the mobile phase groups flows**

**The five-reservoirs mathematical model of the carbothermal process of silicon production in the EAF using a pelletized charge**

Using this algorithm, a mathematical model of the carbothermal process of silicon production was created using a pelletized charge.

Taking into account the chemistry of the silicon smelting process, a scheme of interaction between the flows of mobile phase groups between the reservoirs was compiled [11].

The temperatures of the first and second reservoir are 1530 °C and 1600 °C, respectively. The third reservoir simulates the furnace shaft and maintains a temperature of 2200 °C. The fourth reservoir has a temperature of 1800 °C, which corresponds to the beginning temperature of the silicon exhaust from the EAF. The fifth reservoir imitates the final product (crystallized silicon) [11, 12].

The standard charge in the model was presented by the chemical composition of 17 elements (Si, P, B, Fe, Ca, Al, Ti, Na, Mg, O, H, C, N, K, S, F, Cr) used in the real production of Cheremshansky quartzite, bituminous coal (produced in Kazakhstan and Colombia), petroleum coke, charcoal, coal electrodes of Novosibirsk electrode plant. The consumption index of each component of the lumped charge corresponded to the values adopted at JSC ‘Kremniy’. The ratio of standard and pelletized charge in the model was set to be 9:1.

In the calculation of the equilibrium composition of the multisystem ‘lumped charge – pelletized charge – electrodes – air – melt – slag – gases – crystallized silicon’, the components thermodynamic properties were taken from the ‘Selector’ databases: g_janaf.DB, g_Yokokawa. DB, g_METALL.DB, S_Al_Si_01.DB, s_dump,DB, s_RobieHemingway.DB, s_sprons98.DB.

Thus, the composition of the model is represented by 146 gaseous elements and compounds, 193 solid components, and 58 elements and compounds in the molten state.

3. **Analysis of decision results for five-reservoir mathematical model of carbothermic process**

Gas-dust emissions, formed as a result of chemical interactions between charge components in lower zones of a furnace, enter the first modeled reservoir. The atmosphere, initially present in the 1st reservoir, and the gas phase, formed in the 2nd and 3rd reservoirs, do not exchange dynamic flows of matter with the external environment. The first reservoir is final; it accumulates dust and gas emissions. The atmosphere is consumed in the oxidation and a reduction of silica ash reducing products. If the initial amount of the atmosphere is low, the products of the carbothermal process can be not fully oxidized. Therefore, the amount of atmosphere in the reservoir was chosen empirically.

Feeding charge is carried out in the 2nd reservoir. Considering the load factors, input streams of raw materials were selected taking into account the data on factory experience. Flows of matter between the 2nd and 3rd reservoirs interact so that a part of raw materials (~ 50 %), loaded into the 2nd reservoir, "falls" mechanically into the 3rd reservoir. In this reservoir, the reduction of SiO₂ to SiC begins (the reaction is: SiO₂ + 3 C = SiC₀β + 2 CO), i.e. the model decision results for the reservoir prove the completeness of recovery and silicon extraction.
The main physico-chemical transformations with the maximum extraction and accumulation of silicon occur in the 3rd reservoir (both due to the intermediate reaction course and due to the direct formation of silicon from its oxide in the combustion zone of the voltaic arc) [3, 12].

The 4th reservoir mimics the production of the silicon melt, containing 94.44 mols of the desired product, which corresponds to 91.73 % wt. In practice, the silicon content in the melt is 96–98 % so one can assume that the decision for the five-reservoir mathematical model describes the melting process adequately.

The 5th reservoir is designed to compare the obtained data of the model with crystallized silicon (temperature 25 °C) and has a decision on the chemical composition of the main product: Al₂SiO₅; SiC; FeSi₂; K₂SiO₃; P; Si; TiSi₂; CrSi; Al₂O₃; Ca₃Al₂Si₃O₁₂; BP; NaAlSi₃O₈; and CaAl₂SiO₆. The silicon content was 89.86 mol (or 83.5 % wt.).

The five-reservoir model of silicon production shows the distribution of the main component in five reservoirs, as well as distribution and accumulation of the main impurity elements in the reservoirs (Figure 2).

**Figure 2.** Distribution and accumulation of basic impurities in five reservoirs of the mathematical model

General silicon recovery by the model was calculated as a percentage of the result of extraction for the final EAF work period (30 feed charging cycles) relatively the sum of Si extraction of the final
period across all model reservoirs, amounted to 69.248 %, which indicates adequacy of the model to the actual technological process (this amount in the industry is in average 65–67 % [3, 12]), Figure 3.

Figure 3. The model decision with calculation of the total silicon extraction (69.248 %)

4. Adequacy of the suggested mathematical model

Based on modeling results for the carbothermic process with pelletized charge, made of technogenic raw materials, it was found that iron is accumulated in the first model reservoir, entering the furnace with raw materials in the form of hematite Fe₂O₃ and then reducing due to gaseous CO and passing into FeO and Fe.

Phosphorus in the form of P₂O₅ enters the EAF with reducing ash and then melts under high temperatures. The residual amount of phosphorus can pass from the charge to the melt since its source is apatite coming with ore and melting without decomposition at 1800 °C.

Aluminum, getting into the EAF workspace with quartzite, forms strong bonds with carbon which are blown out of the EAF when exposed to temperatures >2000 °C and reaction gases.

Calcium accumulation occurs at 1800 °C (4th reservoir); after that this component is partially removed as a reaction gas, and part of CaO is released as dust. However, silicides CaSi are formed during the reduction and partially pass into the melt.

Sulfur, getting into the working space of the furnace with a temperature of 1530 °C in the form of pyrite FeS₂, is almost immediately decomposed and removed as volatile compounds with silicon.

Titanium (in the form of sphene, rutile, and ilmenite) is accumulated in the first model reservoir and, being almost immediately reduced (forming strong compounds with carbon), passes into the melt.

Magnesium, the impurity element, is accumulated both in the 3rd and in the 4th of the model reservoirs, forming in a Si melt such compounds with silicon and aluminum as Mg₂Si, Mg₅SiO₄, MgAl₂O₄, and MgSiO₃, and forming CaMgSi₂O₆ during crystallization.

Impurities of potassium and sodium form compounds with silicon in the 5th model reservoir on crystallized silicon in the form of silicates: K₂SiO₅ and NaAlSiO₅.
Boron in the form of various compounds, as well as all the impurities described above, falls into an EAF with charge, but binds to phosphorus at high temperatures and passes into the 5th model reservoir in the form of the BP compound in small amounts.

The elevated carbon content is observed at 1600°C (2nd reservoir); in the remaining model reservoirs, this component is used for reducing oxides.

Study of the phase composition of silicon samples from ‘Kremniy’ JSC by optical-emission analysis using a Phenom-XL scanning microscope (Netherlands) was carried out for comparison of modeling data. According to the analysis, the sample contains inclusions with metals (Ca, Fe, Al, Ti and Zr), as well as oxycarbides (Figure 4).

Based on the given data, it can be assumed that the fixed compound has the \((\text{Fe}, \text{Ti})\text{Si}_2(\text{Al})\) formula since iron is mainly connected to titanium, and aluminum enters the Fe-Ti phase only in small amounts. The presence of calcium can be neglected due to its insignificant content in the inclusion of the metal silicon sample. The presence of an intermediate SiOC phase (Figure 5, b) indicates the processes of not full reduction \[12\]. Low-contained impurities were not found in silicon by this analysis method.

Thus, the results of modeling the chemical composition of crystallized silicon (5th reservoir) showed comparability of the results.

5. Conclusions
The mathematical model of the thermodynamic analysis of the carbothermal process, created using the ‘Selector’ software package, adequately describes the silicon production from silica in ore-thermal furnaces according to the following parameters:

- choice of the phase states of the components involved in the process (the system ‘traditional (lump) charge – pelletized charge – electrodes – air – melt – slag – gases – crystallized silicon’);
- accepted temperature ranges for basic chemical reactions in EAF (1st reservoir – 1530°C; 2nd reservoir (kiln shaft) – 1600°C; 3rd reservoir (kiln shaft) – 2200°C; 4th reservoir (silicon melt) – 1800°C; 5th reservoir (crystallized silicon) – 25°C);
- chemical composition of raw materials in the model and features of reducing agents (quartzite, a mixture of hydrocarbons (coal from Kazakhstan and Colombia, oil coke, and charcoal), electrodes, dust of silicon-production gas cleaning, dust of aluminum-production electrostatic precipitators, liquid glass, screenings of silicon), 17 independent components: Si, P, B, Fe, Ca, Al, Ti, Na, Mg, O, H, C, N, K, S, F, and Cr;
- single charge of raw materials taking into account industrial consumption factors;
- silicon content in the melt (91.73 wt.%);
– content of the main product in the 5th model reservoir – crystallized silicon (83.5 % wt.);
– the ratio of silicon extraction from the product (up to 69.248 % wt.);
– phase composition of impurity inclusions in the melt and crystalline silicon.

6. Acknowledgments
The study was performed on the basis of research project 11.7210.2017/8.9 within the framework of the state task of the Ministry of Education and Science of the Russian Federation.

References
[1] Nemchinova N V, Shumilova L V, Salhofer S P, Razmahnin K K and Chernova O A 2016 Integrated sustainable waste management. Metallurgical industry (Moscow: Academy of Natural Sciences Publ.) p 494
[2] Gasik M I and Gasik M M 2011 Electrothermy of silicon (Dnipropetrovsk: The National Metallurgical Academy Ukraine Press) p 487
[3] Popov S I 2004 Metallurgy of silicon in the three-phase ore-thermal furnaces (Irkutsk: Kremniy JSC Press) p 237
[4] Nemchinova N V, Leonova M S and Tyutrin A A. 2017 Proc. of the Irkutsk St. Techn. Univer. 1(120) 209–217
[5] Kulik D A, Wagner T, Dmytrieva S V, Kosakowski G, Hingerl F F, Chudnenko K V and Berner U R 2013 Computational Geosci. 17 (1) 1–2
[6] Senchenko A E, Aksenov A V and Vasiliev A A 2010 Proc. of the Irkutsk St. Techn. Univer. 1 135–137
[7] Eliseev I A, Nepomnyashchikh A I and Bychinsky V A 2006 Tidings of Higher Educat. Inst. Mater. of Electr. Techn. 4 53–60
[8] Tyutrin A A and Timofeev A K 2012 Application of the mathematical modeling in the study of the metallurgical silicon production and refining processes Actual problems of science and education MPoSAE04 (2012)
[9] Ringdalen E and Tangstad M 2012 The Minerals, Metals & Materials Society (TMS) 195–203.
[10] Gasik M 2013 Handbook of Ferroalloys: Theory and Technology (Oxford: Butterworth-Heinemann) p 536
[11] Nemchinova N V, Leonova M S and Timofeev A K 2016 Proc. of the Irkutsk St. Techn. Univer. 7 (114) 162–171
[12] Katkov O M 1999 Smelting of Technical Silicon (Irkutsk: Irkutsk State Technical University)