Extraction of Silicon From Silica Sand by Carbothermic Reduction in Mini DC-EAF

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Abstract. This study explores silicon extraction from silica sand using different carbon sources: graphite powder, coke, and coconut shell charcoal. Experiments were conducted to assess the influence of carbon source variation and briquetting on metallic silicon production. The silica sand sample was characterized using X-ray fluorescence, while proximate analysis was performed on the coke and coconut shell charcoal reductants. Each experiment used 50 grams of silica sand with varying amounts of carbon sources at a C:SiO_2 mole ratio of 1.8:1. The reductants were tested both with and without briquetting using a DC electric arc furnace for 10 minutes. SEM-EDS and X-ray diffraction were employed for result analysis, with comparisons made to other materials. The experiment using coke as a reductant with briquetting yielded the best result with a Si content in the metal of 98.15%. The experiment with a mixture of silica sand and coconut shell charcoal briquette resulted in a SiC product with Si content of 54.46%. The experiment with a mixture of silica sand and graphite briquette resulted in a SiO_2 and SiC product with Si content of 43.17%. The experiment without briquetting using coke as a reductant showed a high SiO_2 content, as seen from the oxygen content of 36.44%. The experiment without briquetting using coconut shell charcoal as a reductant resulted in a SiO_2 and SiC with Si content of 26.64%. The mixture of silica sand and graphite without briquetting produce SiC as a product with Si content of 70.6%.

Keywords : Silicon, silica sand, coke, coconut shell charcoal, graphite powder

1 Introduction

Silicon is the most common semiconductor material used to manufacture solar cells, dominating 95% of the modules sold[1]. Silicon is used as a semiconductor for solar cells because of its high efficiency, low cost, and long lifetime. Silicon semiconductor has the highest energy conversion rate of 25% whereas other industrial cells remain at 15-18% energy conversion rate[2]. 89.9% of silicon semiconductors are made of mono- and multi-crystalline silicon wafers, 7.4% is made of thin film consisting of amorphous Si, CdTe, and CIS, and 2.6% is made of silicon ribbons[3].

Crystalline silicon cells formed a crystal lattice made of connected silicon atoms. This lattice makes light conversion to electricity more efficient[1]. Cells made of crystalline silicon cells are expected to maintain 80% of their original power after 25 years of use. Crytalline silicon photovoltaic (PV) market keeps on increasing every year[4]. This shows that more silicon metal is needed for renewable energy to create a clean environment.

Silicon is mainly produced by carbothermic reduction of silica in a electric arc furnace, in which silica is reduced by carbon bearing material at temperature around 1300 to 2000°C at atmospheric pressure[5] which is the operating condition of industrial submerged-arc furnace.

Silicon plant use around 11-13 MWh of electrical energy to produce one metric ton of silicon[6].

The overall reaction of silica carbothermic reduction is shown below :

$$SiO(g) + SiC(s) = 2Si(s) + CO(g) \quad (1)$$

This reaction is the sum of six possible reactions during silica carbothermic reduction. These six reactions can be specified according to the temperature range of the reactor. All of the possible reaction is shown below[7] :

$$SiO_2 + 2C = Si + 2\ C \quad (2)$$
$$SiO_2(s) + C(s) = SiO(g) + CO(g) \quad (3)$$
$$SiO(g) + 2C(s) = SiC(s) + CO(g) \quad (4)$$
$$2SiO_2(s) + SiC(s) = 3SiO(g) + CO(g) \quad (5)$$
$$SiO(g) + SiC(s) = 2Si(s) + CO(g) \quad (6)$$
$$SiO_2(l) + Si(l) = SiO(g) \quad (7)$$

In Indonesia, silica sand is commonly found. Half of Indonesia is mostly covered by acidic igneous that consist of at least 63% of silica sand (SiO_2)[8,9]. Indonesia's reserve of silica sand is estimated to be around 4.55 billion tonnes. Despite this much silica sand reserve, Indonesia is still unable to produce silicon on its own.

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2 Materials and methods

2.1 Materials

The raw materials used are silica sand from PT Timah Investasi Mineral, graphite powder, coke, and coconut shell charcoal. Coke and coconut shell charcoal were analyzed using proximate analysis to determine the fixed carbon content as shown in Table 1 and Table 2.

Table 1. Proximate analysis result of coke

Content	Moisture	Ash	Volatile Matter	Fixed Carbon
%adb	0.804	11.97	9.524	77.692

Table 2. Proximate analysis result of coconut shell charcoal

Content	Moisture	Ash	Volatile Matter	Fixed Carbon	Sulphur
%adb	7.01	1.95	16.57	74.47	0.02

Silica sand was analyzed using X-ray fluorescence analysis (XRF) to determine SiO_2 content as shown in Table 3.

Table 3. Composition of the silica sand by XRF

Remarks	Content (Wt%)
SiO_2	98.05
Al_2O_3	0.87
Fe_2O_3	0.49
K_2O	0.08
TiO_2	0.03
Cr_2O_3	0.07
H_2O	0.34
ZrO_2	0.08

2.2 Methods

2.2.1 Materials preparation

Graphite powder with a high carbon content of 99.99% was obtained in a fine condition, ready for use in the experiment. However, the silica sand, coke, and coconut shell charcoal were received in a coarse condition. To prepare them for the experiment, a portion of each material was grinded to a particle size of -45 mesh.

The grinding process was carried out at the Mineral Processing Laboratory of Metallurgical Engineering ITB using a ball mill. The ball mill's rotation speed was set between 116.7 and 122.7 rpm, and the grinding was conducted for 15 minutes to achieve the desired particle size.

After grinding, the materials were sent to different laboratories for further analysis. The XRF analysis, which determines the elemental composition of the materials, was conducted at the Hydrogeology and Hydrogeochemistry Laboratory, Mining Engineering ITB.

Additionally, the proximate analysis, which provides information about the material's moisture, volatile matter, fixed carbon, and ash content, was carried out at The Laboratory for Mineral and Coal Analysis, Department of Metallurgical Engineering, Bandung Institute of Technology.

2.2.2 Carbothermic reduction of silica sand

The carbothermic reduction of silica sand was carried out using a laboratory-scale DC electric arc furnace at the Laboratory of Pyrometallurgy, Bandung Institute of Technology. The experimental setup involved inserting a briquette into a graphite crucible. This briquette contained a mixture of silica sand and a reducing agent, with a molar ratio of C:SiO_2 of 1.8:1. The reducing agents used in the experiments were coke, graphite powder, and coconut shell charcoal.

Both the silica sand and the reducing agent inside the briquette were of a particle size fraction of -45 mesh. To bind the mixture, a small amount of starch (0.01 wt%) was added as a binding agent.

Once the mixture was prepared in the graphite crucible, the crucible was placed inside the direct current electric furnace. The graphite electrode was then gradually lowered until an arc was formed. The heating process was conducted for a duration of 10 minutes.

To investigate the effect of briquetting, additional experiments were carried out using the same parameters but without briquetting the sample.

2.2.3 Product analysis

The metallic product obtained from the experiment was subjected to energy-dispersive X-ray spectroscopy (EDS) analysis. EDS is a technique used to determine the elemental composition of a material by measuring the characteristic X-rays emitted when the material is bombarded with electrons. This analysis helps identify the presence of various elements in the metallic product, including silicon and carbon, which are relevant to the study. On the other hand, the residue left after the experiment was subjected to X-ray diffraction (XRD) analysis.

3 Results and discussion

3.1 Weight loss during experiment

Table 4 presents the weight change data for each experiment. The initial weight and final weight represent the combined weight of the graphite crucible, silica sand, reducing agent, and graphite electrode before and after the experiment, respectively. The mass loss observed during the experiment can be attributed to several factors.

Firstly, the formation of SiO gas and CO gas during the reduction process contributes to the overall mass loss. These gases are produced as a result of the chemical reactions taking place between the silica sand and the reducing agents.

Secondly, the loss of volatile matter and moisture present in the coke and coconut shell charcoal also adds to the reduction in mass. These volatile components are released as the materials are heated, leading to a decrease in weight.

Additionally, the reduction of the graphite electrode itself during the heating process also plays a role in the observed mass loss. As the graphite electrode participates in the reduction reactions, it undergoes chemical changes, resulting in a reduction in its mass.

Table 4. Summary of weight change of carbothermic reduction of silica

Reducing Agent	Briquette	Initial weight (gram)	Final weight (gram)	Weight change (%)
Graphite Powder	No	977	933.3	4.46
Coke	No	1003.6	965.4	4.28
Coconut Shell Charcoal	No	1028.6	982.9	4.44
Graphite Powder	Yes	960.4	918.3	4.42
Coke	Yes	991.5	929.5	5.06
Coconut Shell Charcoal	Yes	998.8	961.7	3.74

3.2 Phases in products

Fig. 1 presents the Si-C binary phase diagram, which was constructed using the FactSage thermodynamic simulation application. The diagram is based on data obtained at a pressure of 1 atm and temperatures ranging from 1000°C to 4000°C, considering a molar ratio of C/(Si+C) from 0 to 1. The Si-C binary diagram illustrates all potential phases that can result from the reactions between silicon and carbon. Notably, the diagram indicates that carbon cannot dissolve in metallic silicon, except in the form of SiC (silicon carbide). The phases that can be formed from these reactions are Si+SiC, Si+gas, C+gas, gas, and C+SiC. Therefore, if metallic silicon is found in the products, any carbon detected through EDS analysis would be attributed to SiC or residual carbon that has not undergone complete reaction. In other words, the presence of carbon in the final product can be explained by its existence in the form of SiC or unreacted residual carbon.

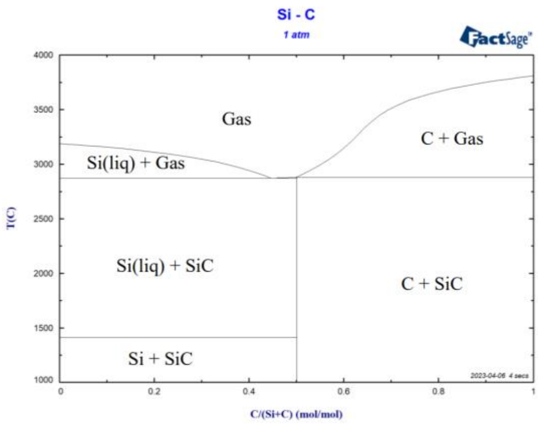

Fig. 1. Si-C binary phase diagram

The XRD analysis was employed to identify the crystalline phase of the solid calcine, aiming to comprehend the minerals that form in the residue powder. Fig. 2 displays the XRD analysis results of the experiment with briquetting, while Fig. 3 shows the XRD analysis results without briquetting.

In both graphs, silica and carbon peaks are evident, indicating that the carbothermic reduction process has not been completed even after 10 minutes. Silicon carbide (SiC) was formed as an intermediate product, as observed in the graph.

The analysis also revealed the presence of residual carbon and SiO_2 that have not reacted in the residue, despite silicon having already formed. These observations indicate that the reduction process is not yet finished, and some reactants remain unreacted in the final product.

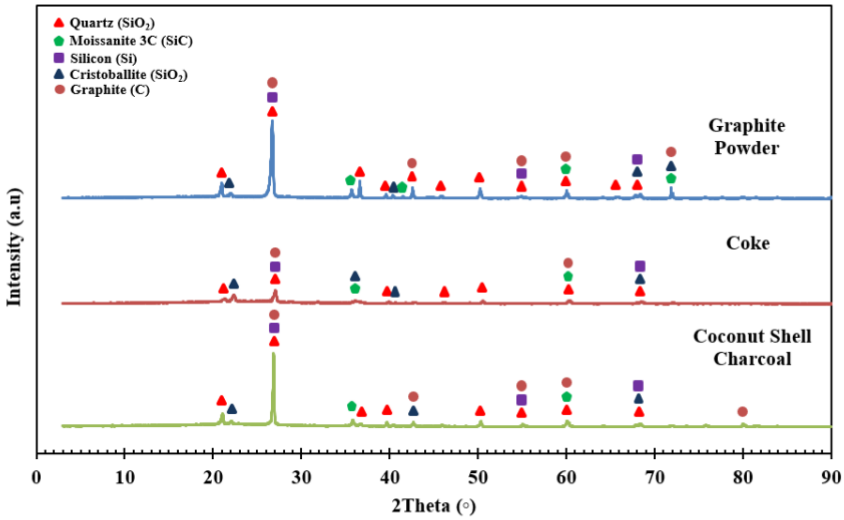

Fig. 2. XRD analysis of experiment with briquetting

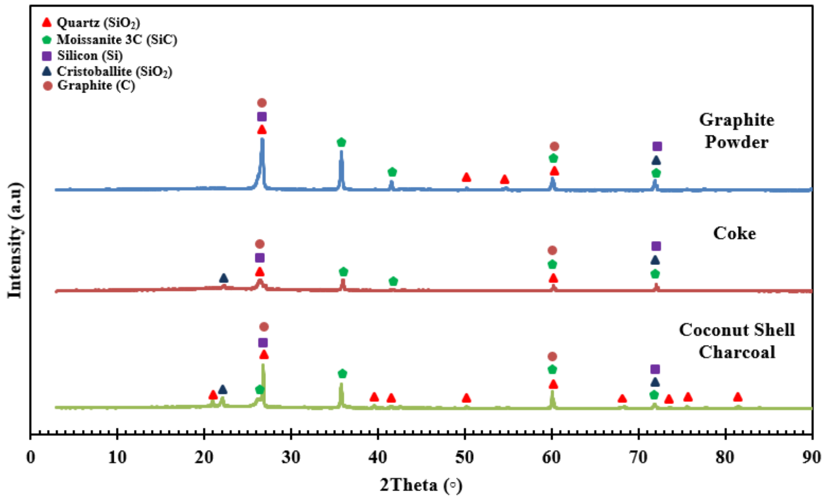

Fig. 3. XRD analysis of experiment without briquetting

3.3 Products analysis

The analysis of the product was conducted to determine its chemical composition and verify whether silicon has formed or not. This was accomplished by observing the percentage of silicon and carbon in the product. It is essential to monitor carbon because it can lead to the formation of SiC as illustrated in Eq. 4 and Fig. 1. Fig. 3 displays the elemental mapping image, while Fig. 4 exhibits the backscattered image obtained through SEM-EDS of the silicon product in the experiment using coke as the reducing agent with briquetting. In the region where silicon is concentrated, EDS analysis was performed at points "1," "2," and "3.Table 5 shows the EDS analysis results of the silicon product in the experiment using graphite powder with briquetting.

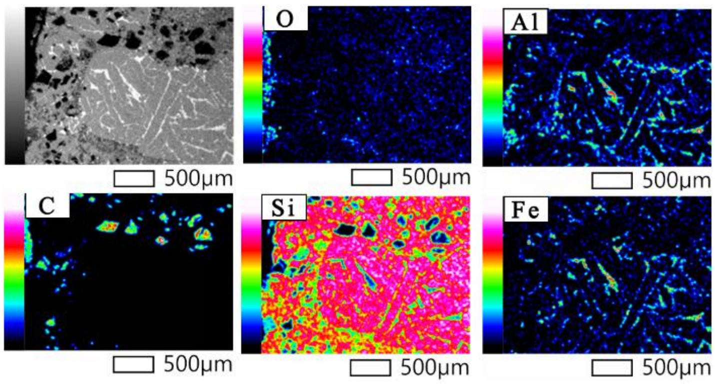

Fig. 4. Elemental mapping of the silicon product in the experiment using coke with briquetting

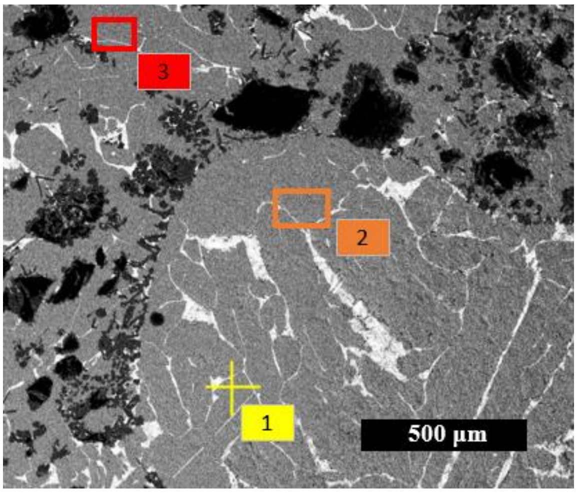

Fig. 5. Backscattered image of the silicon product in the experiment using coke with briquetting

Table 5. EDS analysis results of the silicon product in the experiment using coke with briquetting

Point	Weight Percent				
	C	O	Si	Al	Fe
1	15.23	0.83	83.94	-	-
2	13.24	1.08	85.68	-	-
3	12.10	1.12	86.19	0.26	0.33
Average	13.45	1.01	84.95	0.26	0.33

Table 6. Summary of average weight percent of element from EDS results in all experiments

Reducing Agent	Briquette	Magnification	Weight Percent					
			C	O	Si	Al	Fe	Mg
Coke	Yes	50x	13.45	1.01	84.95	0.26	0.33	-
Graphite Powder	Yes	50x	39.77	9.44	43.17	5.85	1.77	-
Coconut Shell Charcoal	Yes	50x	44.89	0.66	54.46	-	-	-
Coke	No	50x	11.12	36.44	52.09	0.36	-	-
Graphite Powder	No	50x	28.59	0.81	70.60	-	-	-
Coconut Shell Charcoal	No	150x	26.64	15.24	51.73	6.27	-	0.12

The experiment using different parameters was also analyzed using SEM-EDS with the same method. Table 6 shows the summary of the average weight percent of element presents in the EDS analysis.

The experiment utilizing coconut shell charcoal without briquetting is conducted at 150x magnification due to the inability to identify the concentrated domain of silicon at 50x magnification. The mixture of coke and silica sand briquettes demonstrate the ability to reduce silica sand more effectively compared to briquettes made from silica sand mixed with coconut shell charcoal and graphite powder. Silicon has been formed in all experiments, as observed from Fig. 2 and Fig. 3. However, it is noteworthy that in the experiment utilizing a mixture of coke and silica sand briquettes, a substantial amount of silicon was generated, evident from the silicon's weight percentage of 84.95%. Table 7 shows the silicon content in the metals by disregarding the carbon content.

Table 5. Weight percent in the metal of the silicon product in the experiment using coke with briquetting

O	Si	Al	Fe
1.16	98.15	0.30	0.38

The experiment involving briquetting with graphite powder and coconut shell charcoal resulted in the formation of SiC as the product. On the other hand, the experiment using coke without briquetting was not able to effectively reduce the silica sand, as indicated by the high oxygen content (36.44%). Similarly, the experiment using coconut shell charcoal produced SiC as a product, but there was still a significant amount of silica sand that remained unreduced. The experiment using graphite without briquetting resulted in the final product containing silicon carbide and silicon, as evidenced by the silicon content, which was measured at 70.6%.

The presence of moisture and volatile matter in the briquettes can significantly impact their porosity during the heating process[10]. This, in turn, influences the interaction of the formed SiO gas with carbon or SiC (silicon carbide), ultimately enhancing the production of silicon metal. Specifically, coconut shell charcoal contains 7.01% moisture and 16.57% volatile matter, while coke contains 0.804% moisture and 9.524% volatile matter, and graphite powder has no moisture or volatile matter.

Due to the higher moisture and volatile matter content in coconut shell charcoal compared to coke, more energy is required to evaporate these components. Consequently, the reduction process in silica sand briquettes with coke takes longer than in briquettes with coconut shell charcoal.

The use of graphite powder in briquettes is not as effective in reducing silica sand due to its lack of moisture and volatile matter, leading to poor porosity in the briquettes. As a result, SiO gas finds it difficult to diffuse through the briquettes and make contact with carbon or SiC to form silicon metal. However, when graphite powder is used without briquetting, it can efficiently reduce silica sand. The absence of briquetting allows the SiO gas to flow through the gaps between each particle, enabling better interaction with the high carbon content (99.999%) of the graphite powder.

Comparatively, both coke and coconut shell charcoal have lower carbon content than graphite powder, which diminishes their reduction capabilities when used without briquetting. In such cases, the SiO gas formed is more likely to be expelled. Therefore, a higher carbon content improves the effectiveness of the reduction process when briquetting is not employed.

4 Conclusions

This research focuses on comparing the effectiveness of different carbon materials and the impact of briquetting in the carbothermic reduction of silica. It has been observed that both coke and coconut shell charcoal exhibit enhanced silica sand reduction when used in briquetted form. This improvement can be attributed to the presence of moisture and volatile content in these carbon materials, which contribute to the formation of porosity within the briquettes during the reduction process. The increased porosity facilitates better contact between the SiO gas formed and the carbon and SiC present, leading to more efficient reduction. On the other hand, graphite powder demonstrates superior reduction effectiveness when used without briquetting. This is mainly due to its high carbon content, which allows for more effective reduction reactions. In the absence of briquetting, the SiO gas can easily flow through the gaps between particles, and the porosity resulting from the evaporation of moisture and volatile content does not significantly affect the contact between SiO gas and carbon or SiC.

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