

## OPTIMIZATION OF SILICON EXTRACTION FROM TANJUNG TIRAM ASAHAN NATURAL SAND THROUGH MAGNESIOTHERMIC REDUCTION

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### ABSTRACT

We carried out silicon extraction from the natural resources of Tanjung Tiram Asahan, Batu Bara Regency, North Sumatra through variation of heating temperatures and magnesiothermic reduction. Prior to the extraction, the sand from the natural resource was refined until the solid white silica powder was separated. The reaction conditions were performed at various heating temperatures in a furnace, as follows: at 750 (2 hours), 800 (3 hours), 850 (3 hours), 900 (3 hours), and 950 (3 hours). Optimization of the extraction reaction conditions was then performed using magnesiothermic reduction at several silica and magnesium ratios, i.e. 1:1.125, 1:1.50, 1:1.75, 1:1.20, and 1:1.25. The refined silica, together with all of the silicon products from the extraction, was characterized using XRD and analyzed. The morphology of the reaction product was characterized using an electron microscope. The results showed that changes to the silicon products after extraction varied, depending on temperature. Optimization of silicon extraction from silica was obtained at 800°C for 3 hours, with a silica and magnesium ratio of 1:1.75.

*Keywords:* Magnesiothermic reduction; Natural Sand; RIR Method; Silica; Silicon

### 1. INTRODUCTION

Silicon (Si) is the second most common element in the Earth's crust after oxygen (Lutgens & Tarbuck, 2000). Despite its abundance, this element cannot be found freely. Most of the time, silicon compounds are found in the form of minerals such as silicates ( $\text{SiO}_2$ ) and aluminum silicate ( $\text{Al}_2\text{SiO}_3$ ) (Lee, 1994). To obtain silicon from its minerals in rocks and sand in the form of a single element, it should be isolated and purified from those minerals.

Pure silicon is a metalloid that has properties of metals and non-metals; these lower its conductivity while enhancing its insulation properties (Ergul, 2010). Silicon can form a coordination number of four; it is quite stable and resistant to nucleophilic attack, so it is widely used in many applications (Schubert & Husing, 2004). In the forms of mesoporous silica, this material can be applied in various fields to be used as catalysts (Li et al., 2007), adsorbent materials (Yan et al., 2006), and drug delivery and biosensors (Slowing et al., 2007). In the form of high purity silicon, this material is used in many applications such as in semiconductor

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factories, computer microchips, and solar cells (Saga, 2010). In combination with carbon to form silicon carbide, this material is wear-resistant when used in cutting and crushing equipment, whereas in the form of polymers it can be used as waterproof clothing (Deqing & Ziyuan, 2003).

Several investigators have isolated silicon from its minerals. For examples Zulehner et al. (1993) extracted silicon from quartz by using carbon at a temperature of 2400 K in an electric furnace, with high purity results, while Das et al. (2002) used aluminum as the reducing agent for application in the field of composite materials, as well as by using calcium at a temperature of 720°C. Mishra et al. (1985) reduced pure SiO<sub>2</sub> and SiO<sub>2</sub> slabs electrochemically using fused CaCl<sub>2</sub> and/or CaCl<sub>2</sub>-NaCl salt mixture. Silicon has been isolated from silica fume that is derived from metallurgical grade silica manufacturing residues, using the magnesiothermic reduction method (Sadique, 2010), whereas Bao et al. (2007) synthesized silicon nanocrystal from SiO<sub>2</sub> by using magnesium gas at a temperature of 650°C, in which reduction occurs on the silica surface on the inside and forms a mixture of MgO and silicon.

There are several methods of reducing silica into silicon: carbothermic reduction, aluminothermic reduction, calciothermic reduction, and magnesiothermic reduction (Sadique, 2010). Magnesiothermic reduction is frequently the method of choice, due to its simple process and relatively low temperature.

Thermodynamically, magnesiothermic consideration can be used to reduce silica (SiO<sub>2</sub>) to produce silicon through the following reaction (Sadique, 2010):



The reaction may involve formation of Mg<sub>2</sub>Si in the early stages, followed by reduction of SiO<sub>2</sub> by Mg<sub>2</sub>Si via the following chemical reactions:



In the presence of excess Mg in the reactants, however, additional Mg<sub>2</sub>Si may form by consuming elemental silicon, via the reaction:



In this instance, Equation 3 becomes the preferred reaction, and the condition in which Equation 4 occurs during reaction should be avoided.

In North Sumatra, mainly along the east coast, millions of tons of quartz sands are found; these have not yet been fully utilized, except for molding and pottery purposes. To increase the economic value of this natural sand, it is necessary to perform optimization of the silicon extraction. In this report, we present and discuss the optimization of reaction conditions to obtain silicon, by varying the heating temperature and the ratio of silica and magnesium.

## 2. EXPERIMENTAL METHODS

The raw material, in the form of natural sands, was collected from Tanjung Tiram, Asahan, Batu Bara Regency, North Sumatra. The magnesium powder was purchased from E-Merck, and the work was conducted in the Basic Science Laboratories FMIPA University of Sumatra Utara and BARISTAM Laboratory, Medan. Structural characterization was performed using an X-ray

diffractometer (XRD, Rigaku MiniFlex 600), and microstructural characterization was performed with a scanning electron microscope (FE-SEM FEI Inspect F50) and transmission electron microscope (TEM JEOL JEM-1400).

### 2.1. Silica Separation

Prior to reducing the silica ( $\text{SiO}_2$ ) into silicon, it was separated from natural sand. This separation was performed to remove metal oxides such as  $\text{Fe}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$ ,  $\text{K}_2\text{O}$ , and  $\text{CaO}$  from the sand, and was carried out using sulfuric acid and the two-flotation method. This method was conducted in two stages, using oleic acid, sorbitol, and amine compounds (Fuerstenaw & Urbina, 1988). The sulfuric acid dissolved impurities in the quartz such as iron oxide, ferrous silicate, and aluminum silicate. Water was added to dissolve water-soluble impurities. The suspension formed was then added to oleic acid; this was used as a collector whereby water-soluble impurities were lifted to the surface through the formation of foam. Meanwhile, the polar part of the collector interacted with the surface of the water. In this instance, the water-soluble impurities were separated, while the silica settled down on the bottom. Silica obtained in forms which had a pure white color was characterized by using X-ray diffraction and further used as a silicon source.

### 2.2. Silica Reduction

Separated natural silica sand, mixed with magnesium powder in a certain ratio (1:1.25, 1:1.5, 1:1.75, 1:20, and 1:2.5) was put in a metal vessel and stirred until homogeneously blended; the vessel was then sealed properly. The vessel was heated at a temperature of  $750^\circ\text{C}$  in a furnace for 2 hours. The mixture was cooled and refined using acid leaching methods in three stages. Any intermediates that formed, such as  $\text{MgO}$ ,  $\text{Mg}_2\text{Si}$ ,  $\text{Mg}_2\text{SiO}_4$ , and  $\text{SiO}_2$ , were separated. In the first stage, leaching was done by adding 150 mL 2 M HCl; the mixture was then stirred and heated at  $80^\circ\text{C}$  for 3 hours. The reaction mixture was separated, and the solid product washed with doubly distilled water and dried. The second stage was accomplished by adding a 1:2 mixture of 2 M HCl and 25%  $\text{CH}_3\text{COOH}$ . The mixture was stirred at  $80^\circ\text{C}$  for 3 hours, and the solids were separated, washed with doubly distilled water, and dried. The third stage was performed by adding a 1:2 mixture of hydrofluoric acid and 4.8% acetic acid ( $\text{CH}_3\text{COOH}$ ); the mixture was again stirred and heated at a temperature of  $80^\circ\text{C}$  for 2 hours. The solids were again separated, washed repeatedly with doubly distilled water, and dried at a temperature of  $750^\circ\text{C}$ . In order to study the effect of temperature on the silicon's purity, variations in heating temperature were applied at 800, 850, 900, and  $950^\circ\text{C}$ . The silicon products were then characterized using X-ray diffraction and an electron microscope.

## 3. RESULTS AND DISCUSSION

### 3.1. Silica Separation

Silica separation from natural sand was performed using sulfuric acid and two flotation stages that used oleic acid, sorbitol, and ethylene diamine; the silica was then washed repeatedly with distilled water to produce a white solid product, as seen in Figure 1. After separation, the silica product was characterized using X-ray diffraction; the result is given in Figure 2. The X-ray diffraction pattern was then analyzed. For technical reasons, X-ray characterization of the as-collected sand was not performed. Table 1 The condition of process by adding ST at Concentrations from 0–5 wt % and the ratio of DPNR to M = 70:30 wt%



Figure 1 Quartz sands from Tanjung Tiram, Asahan: (a) prior to separation; (b) after separation

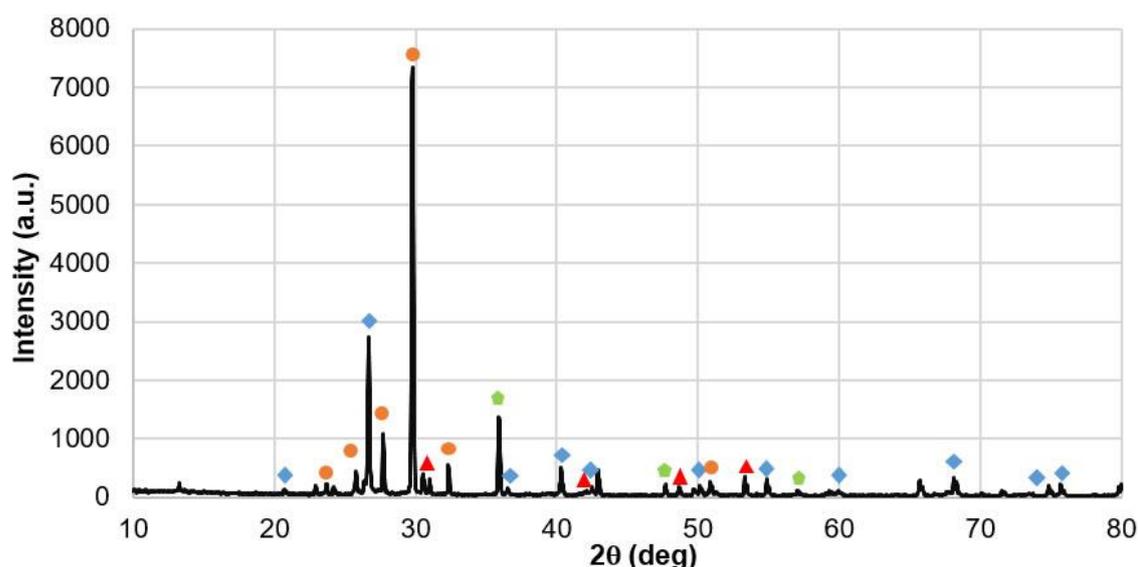


Figure 2 X-ray diffractogram of silica, after separation from natural sand, collected from Tanjung Tiram Asahan, North Sumatra. The symbols  $\blacklozenge$ ,  $\bullet$ ,  $\blacktriangle$ , and  $\blacklozenge$ , refer to  $\text{SiO}_2$ , orthoclase, albite, and muscovite, respectively

There are many ways in which data analysis can be performed through X-ray diffraction patterns. One of the quickest ways is to measure the integrated intensity of the strongest peak in each phase, before converting these intensity values to weight percent by using the reference intensity ratio (RIR) method (Hubbard et al., 1976; Hubbard & Snyder, 1988; Snyder, 1992). In this method, the relationship can be rationalized by substituting the approximate expression for  $F_{hkl}$  in Equation 1 for the expression in Equation 2:

$$F_{hkl} \approx F_{000}(\theta) \approx k * \text{Mol. Wt.} * Z \quad (5)$$

where  $F_{000}(\theta)$  is  $F_{000}$  adjusted for the fall-off of the scattering factor at  $\theta$ ,  $k$  is a constant, Mol. Wt. is the molecular weight, and  $Z$  is the number of molecules or formula weights in the unit cell. Based on this equation, the expression for the RIR,  $I/I_c$ , will be given by Equation 2,

$$\frac{I}{I_c} = \frac{\kappa * F_{hkl}^2 * Lp(\theta) * m_{hkl}}{(V^2 * \rho)} \quad (6)$$

where  $\kappa$  is a constant depending on the standard used,  $F$  is structure factor,  $hkl$  is reflection indices,  $L_p$  is Lorentz-polarization factor,  $m$  is reflection multiplicity,  $V$  is cell volume, and  $\rho$  is density. The results of this calculation for the silica after separation are given in more detail in Table 1.

As can be seen from Table 1, the resulting product after separation was not pure silica. Only a portion was silica (34%), while the rest, although it contained silica, also contained other minerals from a mixture of aluminum, potassium, and sodium oxides.

Table 1 Material composition after flotation of natural sands collected from Tanjung Tiram Asahan, North Sumatra.

Phase name	Chemical Formula	Content (wt.%)
Orthoclase	$K(AlSi_3)O_8$	39.00
Silicon oxide	$SiO_2$	34.00
Albite high	$Na(AlSi_3O_8)$	23.00
Muscovite	$KAl_3Si_3O_{10}(OH)_2$	4.00

### 3.2. Silicon Extraction by Heating Temperature Variations

In the temperature variation process, the solid silica gained after separation was mixed with magnesium powder in the smelting furnace with temperature variations of 750 °C (2 hours), 800°C (3 hours), 850°C (3 hours), 900°C (3 hours), and 950°C (3 hours). There was the possibility that impurities, in the form of compounds other than silica, could be formed during the heating process. These compounds, such as MgO, Mg<sub>2</sub>Si, Mg<sub>2</sub>SiO<sub>4</sub>, and unreacted SiO<sub>2</sub>, needed to be removed in order to obtain pure silicon. These impurities were removed by a leaching process in three stages.

In the first stage, 2 M HCl was added and, after the product was washed and dried, we obtained solids in the form of a grayish-black mixture. The solids were separated and washed with doubly distilled water. In the second stage, a mixture of 2 M HCl and 25% CH<sub>3</sub>COOH was added, and the solids obtained were washed with doubly distilled water, again resulting in grayish-black solids. In the third stage, a mixture of 25% CH<sub>3</sub>COOH and 4.8% HF was added and, after being washed in doubly distilled water, products in the form of brownish-black solids were obtained. These solids were calcined at 150°C for 2 hours before being sintered at temperature variations of 750°C, 800°C, 850°C, 900°C, and 950°C. The results can be seen in Figure 3.



Figure 3 Physical appearance of the results after magnesiothermic reduction at: (a) 750°C for 2 h; (b) 800°C for 3 h; (c) 850°C for 3 h; (d) 900°C for 3 h; (e) 950°C for 3 h

The diffractograms of the silicon products obtained at each temperature variation are plotted in Figure 4. The composition of the products was analyzed using the reference intensity ratio (RIR) method, as explained above; the results are given in Table 2.

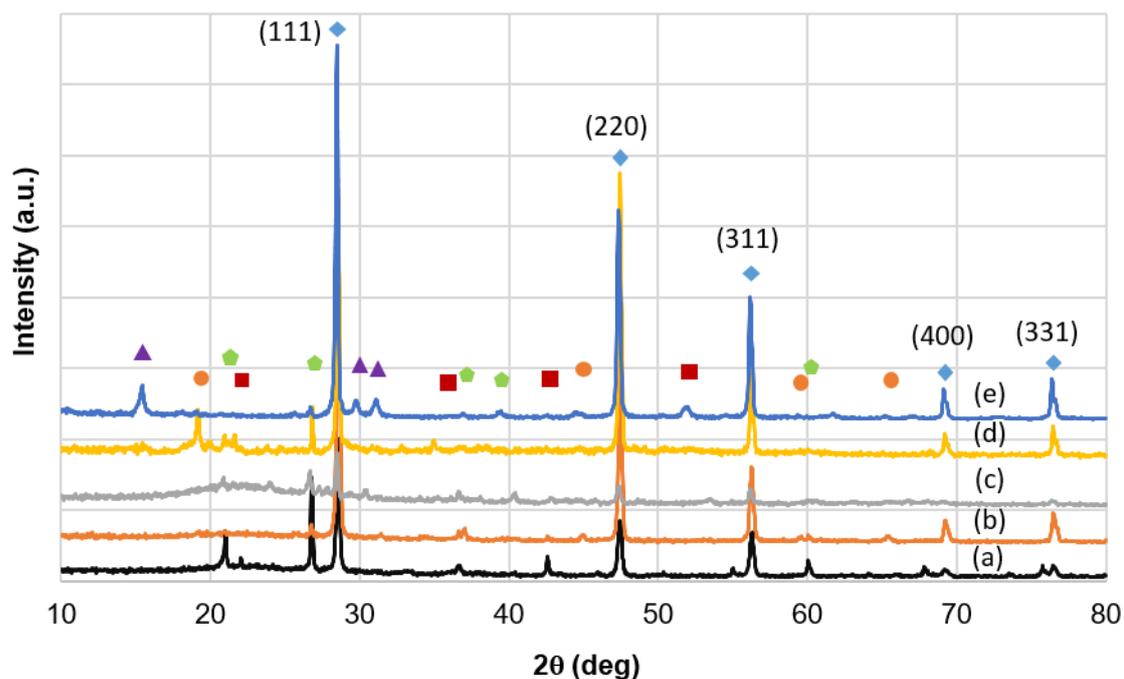


Figure 4 X-ray diffractograms of silicon products at temperature variations of: (a) 750°C (2 hours); (b) 800°C (3 hours); (c) 850°C (3 hours); (d) 900°C (3 hours); (e) 950°C (3 hours). The symbols  $\blacklozenge$ ,  $\blacklozenge$ ,  $\blacksquare$ ,  $\bullet$ , and  $\blacktriangle$  refer to silicon, quartz, cristobalite, spinel magnesia alumina, and ralstonite, respectively. The planes for silicon peaks are given

Table 2 Composition of the products extracted at various heating temperatures

Phase name	Chemical Formula	Content (wt%)
750°C		
Cristobalite-beta high	SiO <sub>2</sub>	8.70
Quartz	SiO <sub>2</sub>	36.00
Silicon	Si	48.00
Magnesium oxide	MgO	1.50
Tridymite - low	SiO <sub>2</sub>	5.80
800°C		
Silicon	Si	85.50
Silicon dioxide	SiO <sub>2</sub>	3.10
Spinel magnesia alumina	MgAl <sub>2</sub> O <sub>4</sub>	11.40
850°C		
Silicon	Si	33.00
Silicon oxide	SiO <sub>2</sub>	59.00
Quartz	SiO <sub>2</sub>	2.00
Periclase	MgO	6.00
900°C		
Tridymite	SiO <sub>2</sub>	16.00
Silicon	Si	79.10
Quartz	SiO <sub>2</sub>	1.90
Cristobalite	SiO <sub>2</sub>	3.00
950°C		
Stishovite	SiO <sub>2</sub>	8.10
Quartz alpha	SiO <sub>2</sub>	39.00
Silicon	Si	52.90

Table 2 shows that the best condition for sintering is a temperature of 800°C for 2 hours, in which the composition of silicon is up to 85.5%. At the same time, the morphology of silicon at temperature variations of 800°C, 850°C, 900°C, and 950°C were characterized using a scanning electron microscope (SEM); the results are given in Figure 5. Under a magnification of 10,000 times, this showed that the shape of the particles of silicon products did not show significant differences under different heating temperatures. The morphology of the extracted products was a spherical particle shape, in the form of granules that formed aggregates.

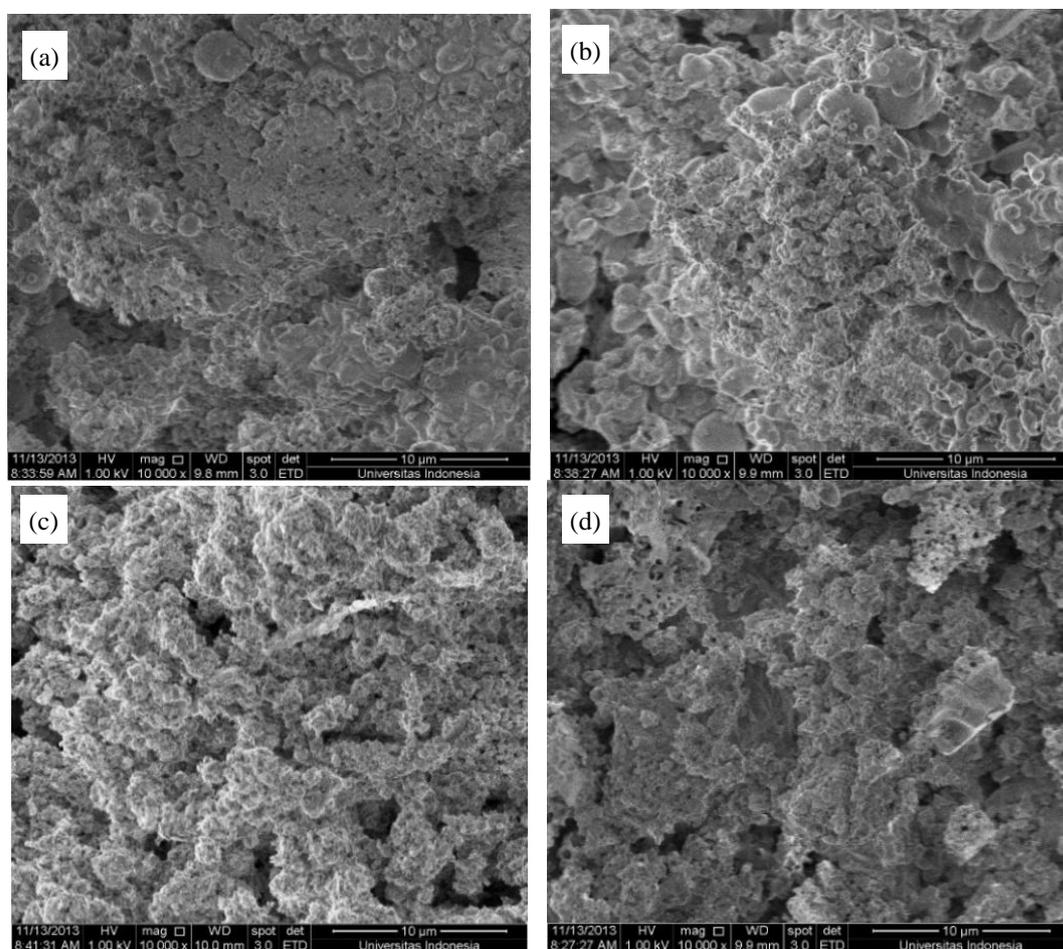


Figure 5 Secondary electron images (SEI) of the silicon products obtained at heating temperature variations of: (a) 800°C; (b) 850°C; (c) 900°C; (d) 950°C. Bar scale is 10 µm

### 3.3. Silicon Extraction with Silica and Magnesium Ratio Variations

In this work, we performed optimization of silicon extraction from silica separated from natural sand by varying the ratios of silica and magnesium at (1:1.25), (1:1.5), (1:1.75), (1:2.00), and (1:2.50). Silicon obtained from the extraction was characterized using X-ray diffraction; the diffractograms at each variation of silica and magnesium ratios are shown in Figure 6. As can be seen, in most of the ratios, the dominant peaks are silicon, except for the ratio of 1:2.00 in which the dominant peak is quartz. It is suspected that at this ratio and sintering temperature, there was an excess of magnesium as stated in Equation 4, resulting in a reduction of the silicon product. Other minor phases are also shown in Figure 6, with more detail given in Table 3.

The purity of silicon under silica and magnesium ratio variations, at a temperature of 800°C for 3 hours, was also analyzed using the reference intensity ratio (RIR) method. The results at ratios of (1:1.25), (1:1.50), (1:1.75), (1:2.00), and (1:2.50) are given in Table 3. It can be seen from the table that the best condition for optimization was a silica and magnesium ratio of 1:1.75.

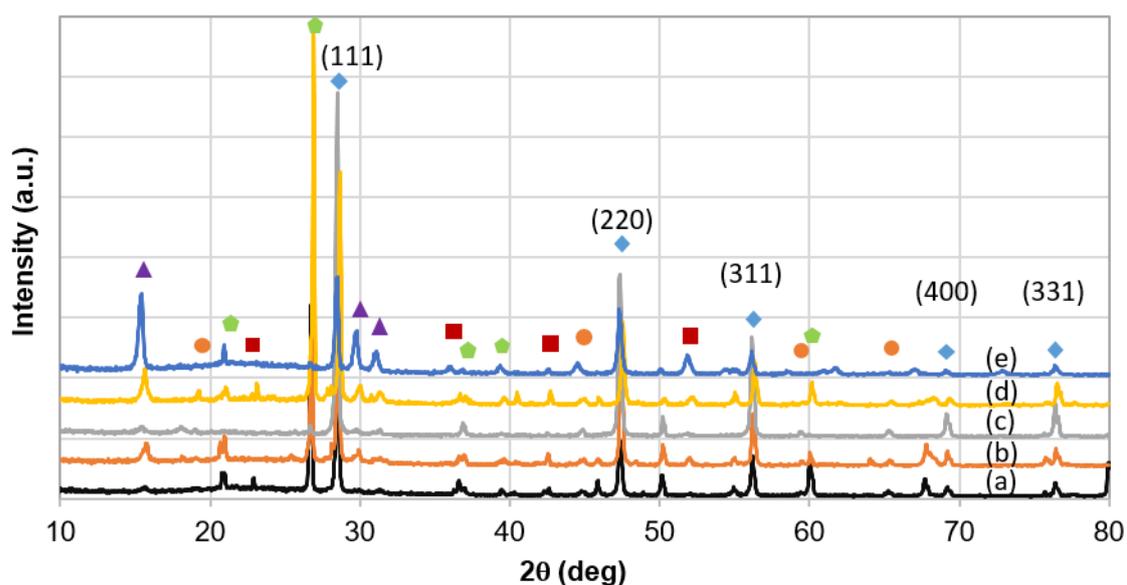


Figure 6 X-ray diffractograms of silicon products heated at 800°C for 3 hours under the following silica and magnesium ratios: (a) 1:1.25; (b) 1:1.50; (c) 1:1.75; (d) 1:2.00; and (e) 1:2.50. The symbols  $\blacklozenge$ ,  $\blacklozenge$ ,  $\blacksquare$ ,  $\bullet$ , and  $\blacktriangle$  refer to silicon, quartz, cristobalite, spinel magnesia alumina, and ralstonite, respectively. The planes for silicon peaks are given

Table 3 Composition of the products extracted at 800°C (3 hours) with various silica and magnesium ratios

Phase name	Formula	Content (wt.%)
<i>Ratio of 1:1.25</i>		
Silicon	Si	39.70
Quartz	SiO <sub>2</sub>	60.30
<i>Ratio of 1:1.5</i>		
Silicon	Si	44.10
Quartz	SiO <sub>2</sub>	40.20
Ralstonite	Na <sub>3</sub> Mg <sub>3</sub> Al <sub>13</sub> (OH) <sub>17</sub> F <sub>31</sub> (H <sub>2</sub> O) <sub>7</sub>	15.70
<i>Ratio of 1:1.75</i>		
Silicon	Si	90.50
Spinel	(Mg <sub>0.47</sub> Al <sub>0.53</sub> )(Al <sub>1.36</sub> Mg <sub>0.53</sub> B <sub>0.11</sub> )O <sub>4</sub>	9.50
<i>Ratio of 1:2</i>		
Silicon	Si	54.60
Quartz low	SiO <sub>2</sub>	14.50
Ralstonite	Na <sub>3</sub> Mg <sub>3</sub> Al <sub>13</sub> (OH) <sub>17</sub> F <sub>31</sub> (H <sub>2</sub> O) <sub>7</sub>	30.90
<i>Ratio of 1:2.5</i>		
Silicon	Si	33.30
Ralstonite	NaMgAl(F,OH)6H <sub>2</sub> O	58.10
Sodium aluminum silicate	NaAlSiO <sub>4</sub>	8.60

#### 4. CONCLUSION

In this work, the silicon composition after extraction varied depending on temperature; at 750°C (2 hours) it was 48%, at 800°C (3 hours) it was 85.5%, at 850°C (3 hours) it was 33%, at 900°C

(3 hours) it was 79%, and at 950°C (3 hours) it was 52.9%. The optimization of silicon extraction from silica at 800°C for 3 hours with silica and magnesium ratio variations was as follows: at 1:1.25 it was 39.7%, at 1:1.50 it was 44.10%, at 1:1.75 it was 90.5%, at 1:20 it was 64.6%, and at 1:2.50 it was 33.30%. Thus, the best condition in this work was a temperature of 800°C for 3 hours with a silica and magnesium ratio of 1:1.75.

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