Production of Magnesium Metal From Calcined Dolomite Via Pidgeon Process

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Abstract
In the present study, the production of magnesium metal from Turkish calcined dolomite via Pidgeon process was studied under the pressure of 1 mbar. In the experiments, Turkish ferrosilicon, calcium carbide, Aluminum was used as reducing agent. Effects of FeSi (90-150 % of stoichiometric requirement of silicon), “CaC₂-Al” addition and time (60-240 min.) were investigated on recovering of metallic magnesium from calcined dolomite (dolime) at the temperature of 1200 °C-1250 °C. Effects of fluxing additive (CaF₂), calcined magnesite and different temperatures on Mg recoveries and concentrations were also studied using with 100 % of stoichiometric requirement of silicon for 180 min. It was found that magnesium recovery increases with increasing FeSi addition, temperature, time, CaF₂ addition and decreases with increasing calcined magnesite additions under the pressure of 1 mbar. CaC₂ and Al can be alternative reductants FeSi for reduction of calcine dolomite.

1. Introduction
Mg is a silver grey metal which has a dense hexagonal crystal structure and it has two valance electrons. Melting point and boiling point of magnesium are 650 ± 2 °C and 1107 ± 10 °C respectively. It has a very low density as 1.738 g/cm³ when it is compared to other structural metals [1]. The consumption of magnesium in many fields, such as aircrafts, rockets and automobile industry, was expected to increase rapidly for the next decade. Because, magnesium has the lowest density in all structural metals and its strength/density ratio is high. It was reported by the USGS in 2015 that the world's total magnesium production was approximately 878,000 t in 2013 and 907,000 t in 2014, thus the annual supply change is about 3%. On the other hand, the world's demand for magnesium increases nearly 10% per year [2,3,4,5].

Dolomite ore is the most important source to produce metallic magnesium. It is a compound of magnesium carbonate and calcium carbonate with a chemical formula as CaCO₃.MgCO₃. It theoretically consists of 45.3% MgCO₃ and 54.7% CaCO₃ by weight. Dolomite is used in various industries such as metallurgy, glass, chemical and paper [6]. The major part of magnesium production is conducted via the Pidgeon Process which is a metallothermic (silicothemic) process [7]. The first gasless metallothermic combustion experiments were conducted by Merzhanov et al. in the middle of 1960s. Metallothermic reduction reactions are highly exothermic. Thus, the propagation of reactions and the yield of reaction products continue in a self-sustaining mode without requiring additional heat [8]. On the other hand, the Pidgeon Process is highly endothermic (ΔH is about 209 kJ mole of Mg), and heat supply is a critical consideration in industrial reactors. Magnesium is in gaseous phase at the temperature which is reduced, and it is collected in the form of crown at the cooling stage of the retort [9]. Pidgeon process is conducted through the silicothermic reduction of calcined dolomite under vacuum atmosphere. Powdered calcined dolomite and ferrosilicon as reductant, with the addition of slight amount of fluor spar (CaF₂) as the catalyst, are mixed prior to the reduction process as raw materials [7, 10]. Morsi et al. investigated to produce magnesium metal from dolomite ore under inert atmosphere in 2002. The highest recovery rate was achieved as 92% when charge is containing 2.5 wt.% CaF₂, CaO/MgO molar ratio was 1.6. Furthermore, Si/MgO ratio was 1.45. The experiment was conducted at 1300 °C for 5 hours. Minic et al. carried out the results of the characterization and thermal analysis of the slag from the magnesium plant named Bela Stena in Serbia. Dicalcium silicate based structure was determined in the solidified slag. Magnesium was mostly in the form of periclase, merwinite and melilite minerals. In 2015, a one-step method, involving dolomite decomposition and magnesium reduction, was examined by Zhang et al. The results showed that the one-step developed technology is
effective for both reducing process duration and saving energy.
Although Turkey has 15,887,160,000 t (detected and probable) of world dolomite reserves [14], there is not any industrial plant for metallic magnesium production yet in Turkey. Yucel et al. investigated the parameters affecting the silicothermic reduction of calcined dolomite using Turkish ores and ferrosilicon sources. In the common silicothermic process, the use of ferrosilicon increases the cost of production. This work aims to reduce the cost of magnesium production by using CaC\(_2\) instead of ferrosilicon as much as possible. CaC\(_2\) is a chemical compound and its most important application areas are fruit ripening and the production of acetylene gas (C\(_2\)H\(_2\)), and it costs approximately half of ferrosilicon [15]. In the experiments, increasing proportion of CaC\(_2\) was used with ferrosilicon. Process duration and temperature were carried out as variables in order to obtain high recovery efficiency ratios. The net reaction between ferrosilicon and dolomite is given with Eq. 1. The reaction for the use of CaC\(_2\) to reduce dolomite gives metallic magnesium of 3 moles as shown in Eq. 2.

\[
\begin{align*}
2\text{MgO} \cdot \text{CaO} + \text{FeSi} &\rightarrow 2\text{Mg} + \text{Ca}_2\text{SiO}_4 + \text{Fe} \quad (1) \\
3\text{MgO} \cdot \text{CaO} + \text{CaC}_2 &\rightarrow 3\text{Mg} + 4\text{CaO} + 2\text{CO} \quad (2)
\end{align*}
\]

2. Experimental Procedure

Calcined dolomite was provided by domestic source in Turkey. It was milled by using a laboratory scale Siebtechnic vibratory cup mill. Particle size of milled dolomite was measured by using Malvern Instruments Mastersizer 2000 particle size analyzer and it is calculated in a large distribution varying from 1.855 \(\mu\)m to 74.715 \(\mu\)m. Particle size distribution of milled calcined dolomite is given in Figure 1. Calcined dolomite was analyzed by using chemical analysis and AAS (Perkin Elmer Analyst 800).

![Figure 1. Particle size distribution of calcined dolomite ore after milling.](image)

Chemical analysis of calcined dolomite is given in Table 1.

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>MgO</th>
<th>Fe(_2)O(_3)</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>Na(_2)O</th>
<th>K(_2)O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>58.57</td>
<td>40.55</td>
<td>0.13</td>
<td>0.45</td>
<td>0.12</td>
<td>0.04</td>
<td>0.03</td>
</tr>
</tbody>
</table>

ETI Elektrometalurji grade FeSi (75.0% Si, 24.0% Fe, 0.1% Ca, 0.9% Al by wt.) was used and ETI Elektrometalurji grade CaC\(_2\) (min. 97.0% CaC\(_2\) by wt.) was also employed as a reductant aiming to reduce the amount of FeSi.

The XRD pattern of calcined dolomite ore was obtained by using PANalytical PW3040/60 XRD. XRD pattern is given in Figure 2. The dolomite ore comprises mainly CaO, MgO and a slight amount of CaCO\(_3\) according to XRD pattern.

![Figure 2. XRD pattern of calcined dolomite ore.](image)

Experiments were carried out in a cylindrical retort which is made from 304 stainless steel. The yield magnesium vapor condenses and forms the crown in the output region of the retort. To obtain vacuum atmosphere in the retort, a two stages integrated rotary vane pump ILMVAC - PK8D used which can hold a final pressure of 2\(\times\)10\(^{-4}\) mbar. ILMVAC PIA 100 piezoelectric sensor was used in order to evaluate the extent of vacuum. The retort was externally heated by using a SiC resistance furnace having a maximum temperature of 1350 °C. The schematic sketch of experimental setup is given in Figure 3.

![Figure 3. Schematic sketch of experimental setup.](image)

The details of the system can be found elsewhere [4]. Reduction experiments were conducted at two different temperatures, 1200 °C and 1250 °C, under vacuum atmosphere. At the end of the reduction, the retort was left in the furnace at the same vacuum values and it was cooled to room temperature. Then, the cover was opened and the
condensed magnesium metal on the cooling section and the residue left in the boat were weighted and analyzed. The degree of Mg metal recovery was calculated from residue and reduced metallic magnesium crown by using two different ways given below.

\[
\text{Mg recovery \% (from residue)} = \frac{[(\text{Mg}\%_0 \times W_0) - (\text{Mg}\%_1 \times W_1)]}{(\text{Mg}\%_0 \times W_0)} \times 100 \tag{3}
\]

\[
\text{Mg recovery \% (from crown)} = \frac{(\text{Mg}\%_2 \times W_2)}{(\text{Mg}\%_0 \times W_0)} \times 100 \tag{4}
\]

Where \(W_0\) is the weight of dolomite, \(\text{Mg}\%_0\) is the weight percentage of magnesium in dolomite, \(W_1\) is the weight of residue, and \(\text{Mg}\%_1\) is the weight percentage of magnesium in residue, \(W_2\) is the weight of crown magnesium, \(\text{Mg}\%_2\) is the weight percentage of magnesium in crown.

In the present study, three experimental sets were developed. In the first set, the change of Mg recovery was investigated with the increase in charge (reactant) weight. The change of Mg recovery with increasing CaC\(_2\) addition rate was carried out in the second experimental set at 1200 °C and 1250 °C. In the last experimental set, the experiments were conducted with increasing CaC\(_2\) addition and in different volumes of retorts as 1 l and 10 l. The experiments with 50 g charge were done in 1 l retort for 360 minutes process duration, other experiments with different charge amounts such as 2000 g, 3000 g and 5000 g were conducted in 10 l retort for 480 minutes process duration. Average process duration was about 2 mbar.

3. Results and Discussion

In the first experimental set, effect of charge amount was investigated on magnesium recovery. 100% stoichiometric calcined dolomite - FeSi powder mixtures were prepared and experiments were conducted in different charge (reactant) amounts varying from 50 g to 5000 g. 50 g and 3000 g charge amounts respectively presented the highest recovery rates which were calculated from residue. The highest recovery was detected for the charge amount of 50 g as 98%. On the other hand, the highest Mg recovery calculated from crown was determined as 90% for the experiment conducted with 3000 g charge amount. Figure 4 shows the change of Mg recovery with the increase in charge weight.

In the second experimental set, the effect of CaC\(_2\) addition and the change of reaction temperature were investigated. In these experiments, stoichiometric FeSi - CaC\(_2\) ratio changed from 100% FeSi - 0% CaC\(_2\) to 50% FeSi - 50% CaC\(_2\). All experiments were conducted under vacuum atmosphere at two different reaction temperatures as 1200 °C and 1250 °C. Figure 5 presents effect of CaC\(_2\) and reaction temperature on Mg recovery rate. The experiments show that CaC\(_2\) addition and lower reaction temperatures decreases Mg recovery rates from 98.2% to 82.0% for CaC\(_2\) addition of 50% at 1250 °C. Because of the highest Mg recovery in the first experimental set, third section of experiments, 3000 g charge and 10 l retort was used in order to produce crown magnesium with CaC\(_2\) addition. Magnesium recovery rates were calculated both from residue and crown. At the end of the experiments, 1 l retort, 10 l retort crown and residue recovery rates were compared in Figure 6. According to Figure 6, the highest Mg recovery was determined for 1 l retort 100% FeSi added experiment as 98.2%. On the other hand, the highest recovery was calculated at 10% CaC\(_2\) added experiment as 95.2% from residue and 94.7% from crown for the experiment conducted in 10 l retort.
Chemical analysis results of all experiments are given in Table 2.

<table>
<thead>
<tr>
<th>Experiment/Tmp., °C</th>
<th>Wght., g</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% FeSi/1250</td>
<td>100% FeSi/1200</td>
<td>6.6</td>
<td>1.4</td>
<td>68.6</td>
<td>1.4</td>
</tr>
<tr>
<td>90%FeSi10%CaC₂/1250</td>
<td>11.0</td>
<td>1.4</td>
<td>68.6</td>
<td>1.4</td>
<td>23.3</td>
</tr>
<tr>
<td>90%FeSi10%CaC₂/1200</td>
<td>11.5</td>
<td>0.7</td>
<td>55.4</td>
<td>1.7</td>
<td>23.3</td>
</tr>
<tr>
<td>80%FeSi20%CaC₂/1250</td>
<td>13.0</td>
<td>0.4</td>
<td>50.1</td>
<td>1.7</td>
<td>23.3</td>
</tr>
<tr>
<td>80%FeSi20%CaC₂/1200</td>
<td>12.1</td>
<td>0.9</td>
<td>61.7</td>
<td>2.6</td>
<td>23.3</td>
</tr>
<tr>
<td>70%FeSi30%CaC₂/1250</td>
<td>13.2</td>
<td>0.6</td>
<td>67.9</td>
<td>2.9</td>
<td>23.3</td>
</tr>
<tr>
<td>70%FeSi30%CaC₂/1200</td>
<td>12.5</td>
<td>1.3</td>
<td>67.9</td>
<td>3.0</td>
<td>23.3</td>
</tr>
<tr>
<td>60%FeSi40%CaC₂/1250</td>
<td>14.0</td>
<td>1.5</td>
<td>61.7</td>
<td>3.7</td>
<td>26.9</td>
</tr>
<tr>
<td>60%FeSi40%CaC₂/1200</td>
<td>12.9</td>
<td>1.4</td>
<td>65.7</td>
<td>3.7</td>
<td>26.9</td>
</tr>
<tr>
<td>50%FeSi50%CaC₂/1250</td>
<td>13.2</td>
<td>0.8</td>
<td>60.1</td>
<td>3.8</td>
<td>26.9</td>
</tr>
<tr>
<td>50%FeSi50%CaC₂/1200</td>
<td>14.1</td>
<td>1.5</td>
<td>61.7</td>
<td>7.0</td>
<td>26.9</td>
</tr>
</tbody>
</table>

The highest MgO amount was obtained in the experiment conducted with 50% FeSi - 50% CaC₂ addition ratio as 6.81%. According to chemical analysis of residues, CaC₂ addition affected amount of MgO in residue but there is not a so much difference between 0%, 10% and 20% CaC₂ addition ratios. These MgO ratios were respectively 0, 1.78 and 1.73.

![Figure 1](image)

Figure 1. The change of Mg recovery calculated with increasing CaC₂ addition rate for different experimental volumes conducted with 1 l and 10 l retorts.

4. Conclusion

Calcined dolomite with FeSi and CaC₂, subjected to reduction process under an average process pressure of 2 mbar, at 1200 °C and 1250 °C temperatures for 360 minutes (in 1 l retort) and 480 minutes (for 10 l retort). According to the results of experimental studies, crown Mg obtained which includes 0.007% Fe, 0.247% Ca and 0.004% Si and trace amount of Al. The highest Mg recovery from residue obtained at the experiment with 50 g charge weight and the use of 100% stoichiometric FeSi as 98.17% at the experiment conducted in 1 l retort at 1250 °C. In the experiments, increasing amount of charge and increasing CaC₂ quantity reduced Mg recovery. For example, the use of 40% CaC₂, at the experiment conducted in 1 l retort, was measured as 89.2%. Thus, when the costs of FeSi and CaC₂ (nearly half of FeSi) are compared, it is clear to understand the use of CaC₂ makes the process economically feasible.

References