Extraction of magnesium from garnierite by carbothermal reduction in vacuum

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Abstract
The aim of the traditional pyrometallurgical processes is to extract nickel and iron in garnierite, but it is difficult to extract magnesium of higher value in minerals. Aimed at solving this problem, the extraction of magnesium from garnierite is proposed and studied in this study. The effects of different reduction temperatures, different reduction times and dosage of CaO additions in experiments were investigated. The experimental results indicate that the extraction rate of magnesium can reach 93.23% when the mass ratio of mineral/reductant is 100:28.3, system pressure is 50 Pa, reduction temperature is 1823 K, and reduction time is 120 min, and, at the same time, the purity of metal magnesium in the condensate can be up to 91.88%. Under these conditions, the extraction rate of magnesium can increase to 99.45% by adding 25 wt% CaO, and the purity of the metal magnesium in the condensate exceeds 90%. CaO as the additive can effectively improve the extraction rate of magnesium and promote the recovery and utilization of magnesium. The mechanism is that CaO replaces –O–Mg– in the –O–Mg–O–Si–O– structure to form free MgO, which is reduced to Mg vapor by carbon and condensed into magnesium metal in the condensation zone to achieve the purpose of removing and collecting Mg from the garnierite. At the same time, the reduced slag is rich in Ni and Fe, which can be used for the extraction of Ni and Fe. Compared with the traditional pyrometallurgical process, the process can extract magnesium from garnierite, and the process is short and its operation is simple, which is a potential technology.

1. Introduction
Nickel is a very important metal that can be used in the fields of stainless steel, chemical products, aerospace and others [1, 2]. Generally, the source of nickel is obtained by smelting nickel-containing minerals, and the most important source of nickel minerals is nickel sulfide and nickel laterite ore, which accounts for 30% and 70% of nickel resources, respectively [3]. In recent years, with the gradual reduction of nickel sulfide ore reserves, nickel laterite ore has attracted the attention of scholars.

Generally, nickel laterite ore can be divided into three types: limonites, saprolites and garnierites [4]. The limonites are suitable for hydrometallurgical processes due to their high iron and nickel content, ranging from 40 to 60 and from 0.5 to 1.7 pct, respectively. The saprolites and garnierites are suitable for pyrometallurgical processes because of their high magnesium content, ranging from 10 to 20 pct [5, 6]. Therefore, a number of pyrometallurgical processes for the utilization of the saprolites and garnierites have been studied. The rotary kiln-electric furnace process (RKEF) has been widely used for the extraction of iron and nickel from garnierites.
Ma et al\textsuperscript{9} successfully produced master alloys containing Fe–Ni–Mo using this method. Ma et al\textsuperscript{10} also studied the solid-state metalized reduction of garnierite for recovering iron and nickel at 1200–250 °C with 8 wt% coal and 7 wt% CaF\textsubscript{2} for 20–40 min, and the recovery rates reached 73.4% and 96.5%, respectively. Li et al\textsuperscript{11} studied the effect of CaO on the recovery of iron during solid-state metalized reduction, and Luo et al\textsuperscript{12} also reported that the reduction temperature could be reduced by adding CaO and that the size of ferro-nickel increased. Zeng et al\textsuperscript{13} developed a process using garnierite and red mud which is mainly composed of CaO, Al\textsubscript{2}O\textsubscript{3}, and Fe, and cast iron composed of 1.5–2 wt% Ni and 0.7–0.8 wt% was produced. Further, Wang et al\textsuperscript{14} studied the effect of CaO on the recovery rates of iron and nickel from garnierite by carbothermal reduction in vacuum, which reached 84.33% and 97.00%, respectively. According to the literature, the purpose of these pyrometallurgical processes is to extract iron and nickel from garnierite; in other words, it is difficult to make use of the magnesium in saprolite and garnierite. Qu et al\textsuperscript{14, 15} analyzed the value of magnesium in garnierite and determined it to be approximately three times that of nickel; therefore, the abandonment of magnesium will make it difficult to maximize the value of garnierite.

Focusing on the problem of the utilization of magnesium in garnierite by pyrometallurgical processes, in this study, the extraction of magnesium from garnierite was performed by carbothermal reduction in vacuum based on the work of Wang et al which is advantageous for the effective utilization of garnierite. The effect of the reduction temperature, the reduction time, and the additive (CaO) dosage were investigated to determine the suitable conditions for the extraction of magnesium. In addition, the behavior of magnesium was analyzed using the experimental data.

### 2. Experimental

#### 2.1. Raw materials

The garnierite used in this study was obtained from Yunnan Province, China. Its chemical composition was detected by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) with Optima 8000 (American, PerkinElmer), and the results are listed in table 1. The results suggest that the content of MgO is fairly high, which accounts for 22.83% of the total mass. At the same time, the contents of nickel and iron are considerably low, accounting for just 0.72% and 12.66% of the total mass, respectively. The x-ray-diffraction (XRD) pattern of the Yunnan garnierite is shown in figure 1, which indicates that the garnierite is composed of quartz (SiO\textsubscript{2}), lizardite ([Mg\textsubscript{3}Al\textsubscript{2}][(Si,Fe)\textsubscript{2}O\textsubscript{5}](OH)\textsubscript{4}), pecoraite (Ni\textsubscript{3}Si\textsubscript{2}O\textsubscript{5}(OH)\textsubscript{4}), and aluminium oxide (Al\textsubscript{2}O\textsubscript{3}). Other elements in minerals were not detected due to poor crystallization or trace amounts. The chemical composition results and XRD patterns are consistent, indicating that the raw materials used in this
study are typical garnierite. The chemical composition of a reductant (coking coal) used in the study was analyzed by chemical analysis, and the results are listed in Table 2. The additive used in this study is CaO (analytically pure, Tianjin Fengchuan Chemical Reagent Technologies Co. Ltd), and its composition is listed in Table 3.

### Table 2. Chemical composition of a reductant (wt%).

| Composition          | Fixed carbon | Ash | Moisture | Volatile matter |
|----------------------|--------------|-----|----------|-----------------|
| Content              | 85.83        | 12.02 | 0.14     | 2.01            |

### Table 3. Chemical composition of CaO (wt%).

| Composition | CaO | Sulfate | Fe  | Chloride | Alkali metal | Others |
|-------------|-----|---------|-----|----------|--------------|--------|
| Content     | ≥98.0 | ≤0.1    | ≤0.015 | ≤0.003 | ≤0.5 | ≤1.36 |

2.2. Experimental procedure

The experimental apparatus used in this experiment is a vacuum reaction furnace, which was designed by Kunming University of Science and Technology, and its details are shown in Figure 2. The temperature of the heating zone was monitored by a sheathed thermocouple inserted into the vacuum reaction furnace. First, the garnierite and reductant were crushed to 100% passing 74 μm. Then, the garnierite was homogeneously mixed with a certain amount of reductant, and the mixture was then briquetted (Φ20 mm × 20 mm) and transferred into a graphite crucible. The crucible was placed in the heating zone of the vacuum reaction furnace, and the graphite heater was initiated to heat until it reached the specified temperature at a heating rate of 10 K min⁻¹. When the temperature dropped to room temperature, the crucible was taken out to obtain the slag and the condensate scraped from the condensation plate for further analysis. The entire experimental process is shown in Figure 3.

In this study, the extraction rate of magnesium is used as the evaluation index and is calculated by the following formula:

\[
\alpha = 1 - \frac{m_2 \cdot \omega(Mg)_2}{m_1 \cdot \omega(Mg)_1} \times 100\%,
\]

where \(\alpha\) is the extraction rate of magnesium, \(m_1\) is the weight of garnierite in raw materials, \(\omega(Mg)_1\) is the magnesium content of garnierite in the materials, \(m_2\) is the weight of the slag, and \(\omega(Mg)_2\) is the magnesium content in the slag.

The crystalline phases of the condensate and slag were analyzed by XRD experiments, which were performed on a Japan Science D/max-R diffractometer with Cu Kα radiation (\(\lambda = 1.5406 \text{ Å}\)). The diffraction angle (2θ) was scanned from 5° to 90° with a scanning rate of 2°/min.
3. Results and discussion

3.1. Thermodynamic basis

Simultaneous differential scanning calorimetry (DSC) and thermogravimetric (TG) (NETZSCH, STA449F3) analysis were performed, and the curve is shown in figure 4. It can be seen from the figure that there are two endothermic peaks, at 352 and 886 K, and an exothermic peak at 1098 K; it can be further seen that the mass does not change after 1098 K. According to the [16, 17] and figure 4, the evaporation of free water, crystallization water and constitution water in the lizardite contributes to the endothermic peaks at 352 and 886 K, respectively. The exothermic peak occurring at 1098 K is due to the crystallization of silicate. Therefore, the garnierite was dried at 1098 K for 120 min to obtain its chemical composition and XRD pattern, as shown in table 4 and figure 5, respectively. It can be seen from figure 5 that the main phases are quartz (SiO₂), forsterite (Mg₂SiO₄), cinoenstatite (MgSiO₃), and ferric oxide (Fe₂O₃). The above results indicate that reactions (1)–(3) occur in the magnesium-containing phase during drying.

Table 4. Chemical compositions of garnierite with dehydration (wt%).

| Composition | SiO₂ | MgO | Fe | Ni | Co | Al₂O₃ | Others |
|------------|------|-----|----|----|----|-------|--------|
| Content    | 44.57| 26.21| 14.54| 0.83| 0.03| 5.25  | 9.4    |

Figure 3. Flow chart of experimental procedure.

Figure 4. TG-DSC curves of garnierite.
3.2. Effect of different reduction temperatures and times

First, the garnierite was dehydrated at 1098 K for 120 min as shown in figure 4. Then, the effect of reduction temperature and reduction time on the extraction rate of magnesium was investigated with a reduction temperature of 1623−1823 K, a reduction time of 0−150 min, a system pressure of 50 Pa, and a mixture of 100 g garnierite with dehydration and 28.3 g of coal. The relationship between the extraction rate of magnesium and the reduction temperature and time is shown in figure 6. As can be seen from figure 6, as the reduction temperature increases, the extraction rate of magnesium increases and reaches a maximum at 1823 K. When the temperature exceeds 1723 K, the extraction rate of magnesium varies greatly, from 44.69% at 1723 K to 93.23% at 1823 K, which indicates that the temperature has a great influence on the extraction of magnesium from garnierite by carbothermal reduction in vacuum. Therefore, the reduction temperature of 1823 K is considered the optimum reduction temperature. Meanwhile, when the temperature is constant, as time increases, the extraction rate of magnesium increases, and the extraction rate of magnesium does not change significantly when it extended from 120 to 150 min: from 93.23% to 95.23% (1823 K), from 44.69% to 45.98% (1723 K), and

\[
\begin{align*}
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 & \rightarrow \text{Mg}_2\text{Si}_2\text{O}_5(\text{amorphous}) \\
+ \text{MgSiO}_3(\text{amorphous}) + 2\text{H}_2\text{O} \\
\text{Mg}_2\text{Si}_4\text{O}_9(\text{amorphous}) & \rightarrow \text{Mg}_2\text{Si}_4\text{O}_9(\text{forsterite}) \\
\text{MgSiO}_3(\text{amorphous}) & \rightarrow \text{MgSiO}_3(\text{cinoenstatite})
\end{align*}
\]
from 30.02% to 29.99% (1623 K). Therefore, the reduction time of 120 min is considered the optimum reduction time.

The XRD patterns of the condensate at different temperatures at 120 min are shown in figure 7. As seen from those patterns, the main phases are Mg, MgO, and Mg$_2$Si. When the temperatures are 1623 and 1723 K, the crystalline phases are characterized by three-phase crystal forms (Mg, MgO, Mg$_2$Si) and the main peak is magnesium [18]. When the temperatures is 1823 K, the crystalline phases are characterized by a two-phase crystal forms (Mg and MgO) and the main peak is also magnesium, which indicates that it is feasible to extract magnesium from garnierite by carbothermal reduction in vacuum. It can be seen from figure 7 that the intensity of the Mg$_2$Si diffraction peak becomes weaker with increasing reduction temperature. Therefore, the contents of silicon and magnesium in the condensate under various temperature conditions for 120 min were determined by colorimetry and ICP-AES, respectively. The aforementioned tests were performed, and the results are shown in figure 8, from which it can be seen that as the temperature increases, the total mass of the collected condensate increases from 0.55 to 11.88 g. Meanwhile, according to the silicon content in the condensate, it is known that the mass of silicon in the condensate does not substantially change, resulting in a decrease of the relative content of silicon. When the temperature increases to 1823 K, the relative content of silicon is only 0.23%. Therefore, it is difficult to detect the phase of Mg$_2$Si by XRD. When the temperature reaches 1823 K, the purity of magnesium can reach 91.88%. It is considered that the reactions (4) — (6) occur during the reduction; in addition, the chemical properties of Mg are active and easily oxidized, and therefore, the MgO phase is detected. The XRD patterns of slag at different temperatures at 120 min are shown in figure 9, from which it can be seen that the diffraction peaks of those main phases (Mg$_2$SiO$_4$ and MgSiO$_3$) disappear gradually, and the intensity of these diffraction peaks is very weak at 1823 K. At the same time, the diffraction peak of SiC was detected, which indicates that forsterite (Mg$_2$SiO$_4$) and cinoenstatite (MgSiO$_3$) may react with the reductant to form SiC, as reactions (4), (5), and (7) show; it may also be that the magnesium silicate in the mineral reacts directly with the
reductant to form SiC, as reactions (8) and (9) show. The above reactions were subjected to thermodynamic calculation under the experimental conditions, and the results are shown in figure 10, from which it can be seen that $\Delta G$ is negative at certain temperatures, which means that the reactions are spontaneous at that condition.

\[
\begin{align*}
\text{Mg}_2\text{SiO}_4(s) + 3C(s) &= 2\text{Mg}(g) + \text{SiO}(g) + 3\text{CO}(g) \quad (4) \\
\text{MgSiO}_3(s) + 2C(s) &= \text{Mg}(g) + \text{SiO}(g) + 2\text{CO}(g) \quad (5) \\
\text{Mg}(g) + \text{SiO}(g) &= \text{Mg}_2\text{Si}(s) + \text{MgO}(s) \quad (6) \\
\text{SiO}(g) + 2C(s) &= \text{SiC}(s) + \text{CO}(g) \quad (7) \\
\text{Mg}_2\text{SiO}_4(s) + 5C(s) &= 2\text{Mg}(g) + \text{SiC}(s) + 4\text{CO}(g) \quad (8) \\
\text{MgSiO}_3(s) + 4C(s) &= \text{Mg}(g) + \text{SiC}(s) + 3\text{CO}(g) \quad (9)
\end{align*}
\]

3.3. Effect of CaO addition

The effect of CaO addition on the extraction of magnesium from garnierite was observed with a reduction temperature of 1623–1823 K, a reduction time of 120 min, a system pressure of 50 Pa, a mixture of 100 g garnierite with dehydration and 28.3 g of coal and a CaO dosage of 0%–25% (mass ratio).

Photographs of reduced slag under different experimental conditions are shown in figure 11. It can be seen from the photographs that when the temperature is 1623 K, the shape of the reduced slag is basically unchanged with the addition of CaO; when the temperature is 1723 K, a melting phenomenon occurred in the reduced slag.
with increasing amount of CaO; when the temperature is 1823 K, the reduced slag is bonded to the graphite crucible and a large number of NiFe particles appear, as indicated by the red circle in figure 11 (photographs (14)–(18)). The relationship between the extraction rate of magnesium and the CaO content is shown in figure 12. With increasing CaO addition, the extraction rate of magnesium generally increases. In addition, as can be seen from figure 12, when 25 wt% CaO is added, the extraction rate of magnesium increases from 30.02%, 44.69%, and 93.23% to 38.59%, 87.58%, and 99.45%, respectively.

It can be seen from figure 12 that with the addition of CaO, the extraction rate of magnesium at 1723 K has the greatest influence, and the influence at other temperatures is small. Therefore, the reduced slag and condensate obtained at 1723 K were detected by XRD to analyze the mechanism of CaO in the reaction, and the results are shown in figures 13(a) and (b), respectively. As can be seen from figure 13(a), the condensate was mainly magnesium, which indicates that the addition of CaO does not affect the structure and the crystalline phases of the condensate and only affects the extraction rate of magnesium. Moreover, according to ICP-AES results, the magnesium content in the condensate exceeds 90%. Otherwise, figure 13(b) shows that with increasing CaO content, new phases (Ca$_2$MgSi$_2$O$_7$) were detected and the phase of forsterite disappeared gradually. Combining with figures 13(a) and (b) indicates that the –O–Mg–O–Si–O– network structure can be broken, forming free MgO, which was removed from the mineral by carbothermal reduction. It is well known

**Figure 11.** Photographs of different CaO additions: (1)–(6), 1623 K; (7)–(12), 1723 K; (13)–(18), 1823 K; amount of CaO is 0%, 5%, 10%, 15%, 20%, and 25% from left to right, respectively; (19)–(21), SEM images of reduced slag with 5%, 15%, 25% CaO at 1823 K at 120 min.

**Figure 12.** Extraction rates of magnesium under different CaO additions.
that silicates slag has a network structure made of \([\text{SiO}_4]^{4-}\) tetrahedral units, and \(\text{Si}^{4+}\) ions are combined through bridging oxygen atoms \((O^6)\). The addition of CaO results in the progressive breaking of the Si–O bonds in the network structure to form non-bridging oxygen atoms \((O^-)\) under vacuum \([19–21]\). In addition, the viscosity of the system can be decreased due to the depolymerization of the network structure, which is beneficial to the extraction of magnesium from the mineral. Therefore, as the amount of CaO increases, the extraction rate of magnesium gradually increases and reaches a maximum, which indicates that the amount of CaO plays an important role in the extraction of magnesium from minerals. Therefore, as the amount of CaO increases, the extraction rate of magnesium gradually increases and reaches a maximum, which indicates that the amount of CaO plays an important role in the extraction of magnesium from minerals. Reactions (10) and (11) occur throughout the process. Reaction (11) can occur under the experimental conditions \([22]\), so that only reaction (10) is subjected to thermodynamic calculation, and the results are shown in figure 14, which indicates that reaction (10) can occur at the experimental temperature. This result confirms that MgO can be efficiently extracted from minerals by the proposed method.

\[
\text{Mg}_2\text{SiO}_4(s) + 2\text{CaO}(s) + \text{SiO}_2(s) = \text{Ca}_2\text{MgSi}_2\text{O}_7(s) + \text{MgO}(s)
\]  

\[
\text{MgO}(s) + \text{C}(s) = \text{Mg}(g) + \text{CO}(g)
\]

According to the above analysis and figure 11, it is considered that when the temperature is high, the addition of CaO can form \(\text{Ca}_2\text{MgSi}_2\text{O}_7\). \(\text{Ca}_2\text{MgSi}_2\text{O}_7\) is a melt under high-temperature and low-pressure conditions, which is the reason for the formation of the melt under the conditions of 1723 and 1823 K. At the same time, CaO promotes the extraction of magnesium from garnierite by destroying the structure of the silicate system in the mineral. Therefore, the addition of CaO can promote extraction of magnesium by carbothermal reduction in vacuum from garnierite. Meanwhile, 25 wt% CaO is considered to be the optimal addition amount.
4. Conclusions

(1) In this study, the extraction of magnesium from garnierite was performed by carbothermal reduction in vacuum. The optimal conditions with no CaO for the experiment are as follows: mass ratio of mineral/reductant, 100:28.3; system pressure, 50 Pa; reaction temperature, 1823 K; reaction time, 120 min. The extraction rate of magnesium reached 93.23% and the purity of metallic magnesium in the condensate reached 91.88%. X-ray diffraction results show that the condensate is mainly magnesium, indicating that it is feasible to remove and collect magnesium by carbothermal reduction in vacuum.

(2) The effect of CaO on the extraction of magnesium from garnierite by carbothermal reduction in vacuum was observed. Experimental results show that the optimal addition amount of CaO is 25 wt%. Under the same experimental conditions (50 Pa, 1823 K, 120 min), the extraction rate of magnesium increased from 93.23% with no CaO to 99.45% in presence of 25 wt% CaO. It is believed that CaO can destroy the tetrahedral structure of the silicate system in the mineral, release the MgO from the mineral, and promote the reaction between MgO and the reductant. In addition, CaO can form the phase (Ca₂MgSi₂O₇) with lower melting point and reduce the viscosity of the system to facilitate the escape of Mg vapor from the slag, thereby promoting the extraction of magnesium during the reaction.

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