

# Production of Magnesium by Vacuum Aluminothermic Reduction with Magnesium Aluminate Spinel as a By-Product

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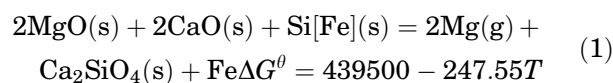
The Pidgeon process currently accounts for 85% of the world's magnesium production. Although the Pidgeon process has been greatly improved over the past 10 years, such production still consumes much energy and material and creates much pollution. The present study investigates the process of producing magnesium by employing vacuum aluminothermic reduction and by using magnesite as material and obtaining magnesium aluminate spinel as a by-product. The results show that compared with the Pidgeon process, producing magnesium by vacuum aluminothermic reduction can save materials by as much as 50%, increase productivity up to 100%, and save energy by more than 50%. It can also reduce CO<sub>2</sub> emission by up to 60% and realize zero discharge of waste residue. Vacuum aluminothermic reduction is a highly efficient, low-energy-consumption, and environmentally friendly method of producing magnesium.

## INTRODUCTION

Magnesium alloys are used widely in the aerospace industry, in the automobile industry, in mechanical engineering, and with portable communication equipment because of their predominant performance having low density,<sup>1</sup> high strength-to-weight ratios, excellent casting capability, good machinability, and good damping characteristics.<sup>2,3</sup> The use of magnesium has great potential in terms of reducing vehicle weight, fuel consumption, and greenhouse gas emissions.

There are two main methods of producing magnesium<sup>4</sup>: molten salt electrolysis and silicothermic reduction. Molten salt electrolysis produces magnesium through the electrolytic reduction of magnesium chloride from brine or the chlorination of hydrated magnesia.<sup>5</sup> Silicothermic reduction is mainly the Pidgeon process that uses FeSi to reduce dolomite in horizontal pots.<sup>6</sup> Prior to the year 2000, molten salt electrolysis was the primary method of magnesium production and the Pidgeon process was a secondary method. Since 2000, because of its low investment and operational costs and easy operation, the use of the Pidgeon process has rapidly grown around the world and especially in China. At present, the Pidgeon process is the main method of magnesium production. The Pidgeon process accounts for about 85% of the world's output of magnesium.

The Pidgeon process uses ferrosilicon as the reductant and calcined dolomite as the magnesium ore, and it produces magnesium through vacuum thermal reduction. The reduction principle of the Pidgeon process is expressed by Eq. 1:



China produces all its magnesium employing the Pidgeon process. In 2014, China's magnesium production capacity exceeded 1.5 million tons and the production quantity exceeded 800,000 tons. Although the Pidgeon process has been well advanced in the past 10 years, magnesium production employing the Pidgeon process still consumes much energy and material and generates much pollution,<sup>7,8</sup> and the energy consumption per unit amount of magnesium metal produced is even higher than that of aluminum metal; it has one of the highest energy consumptions among the nonferrous metallurgy industries.

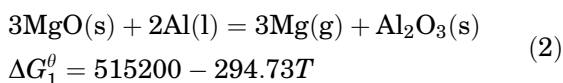
It is difficult to reduce the energy consumption of the Pidgeon process further in the present circumstances. The main reasons are the low content of MgO in materials and low reduction rate of MgO, which lead to greater ferrosilicon and material consumption and a higher ratio of raw material to

rough magnesium. Both are determined by the process principle. If we want to reduce the energy consumption of magnesium smelting, we must develop a new method that increases the content of MgO in raw material, improves the reduction rate of MgO, and decreases the reduction temperature. Producing magnesium by using aluminum as the reductant can reduce energy consumption and the emission of reduction slag and greenhouse gases. The advantages of aluminothermic reduction are many, and they stem mainly from the fact that the reaction is carried out at a relatively low temperature, which is, in fact, the lowest among all thermal processes.<sup>9</sup> Another advantage is that aluminothermic reduction can greatly reduce the ratio of raw material to rough magnesium and improve productivity markedly.<sup>10</sup>

Since discovering the advantages of producing magnesium via aluminothermic reduction, many researchers have focused on the aluminothermic reduction principle. Toguri, Chrisini, and Heggie<sup>11</sup> worked on producing magnesium by using a mixture of calcined dolomite and calcined magnesite with aluminum as a reductant. Similar work was conducted by Guo,<sup>12</sup> Lu,<sup>13</sup> and Rutledge.<sup>14</sup> Their experiments used the same materials but drew different reaction mechanisms. However, all the experiments determined that the aluminothermic reduction could occur below 1000°C and producing magnesium via the aluminothermic reduction can reduce energy consumption by more than 40%. However, none of the aluminothermic reduction methods have been industrialized successfully. The two main reasons are the high cost of aluminum powder and the low utilization rate of reduction slag. If the reduction slag can be sold as a product with high additional value that covers the cost of aluminum powder, the process would have broad potential.

### PRINCIPLE OF A METHOD OF PRODUCING MAGNESIUM BY VACUUM ALUMINOTHERMIC REDUCTION WITH MAGNESIUM ALUMINATE AS A BY-PRODUCT

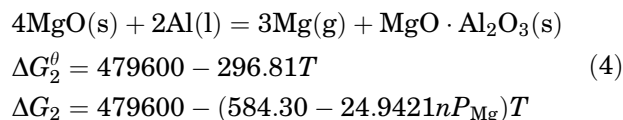
The main composition of magnesite is MgCO<sub>3</sub>, and the main phase of calcined magnesite is MgO. If producing magnesium using aluminum powder as the reductant and using calcined magnesite as materials, the following reaction occurs:



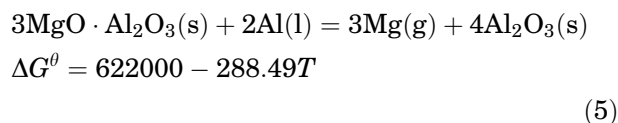
Under a nonstandard condition, the relationship of the Gibbs free energy of Eq. 2 and the equilibrium vapor pressure of magnesium ( $P_{\text{Mg}}$ ) can be described by Eq. 3:

$$\Delta G_1 = 515200 - (582.21 - 24.9421nP_{\text{Mg}})T \quad (3)$$

The equilibrium vapor pressure of magnesium ( $P_{\text{Mg}}$ ) is roughly equal to the residual pressure of the system. The reduction temperature will vary because of different values of  $P_{\text{Mg}}$ , and the theoretical reaction temperature will be below 990 K when  $P_{\text{Mg}}$  is under 10 Pa. Alumina generated in the reduction process is an amphoteric oxide and MgO is a basic oxide, and the two kinds of oxides easily combine to generate a more stable compound, MgO·Al<sub>2</sub>O<sub>3</sub>. The initial reaction that takes place is Eq. 4:



The reduction temperature of MgO further reduces to 910 K when  $P_{\text{Mg}}$  is 10 Pa. If the addition of aluminum exceeds the prescribed dose of Eq. 4, MgO in the form of MgO·Al<sub>2</sub>O<sub>3</sub> that generated in an earlier stage will be partially reduced to metal magnesium (Eq. 5), but the reaction temperature will be higher<sup>15</sup>:



## EXPERIMENTAL

### Materials

The process of producing magnesium uses magnesite as the raw material and aluminum powder as the reductant. The main constituents of magnesite taken from Dashiqiao in China are listed in Table I. Aluminum powder is produced from pure aluminum, and it contains more than 99.5% aluminum element.

### Experimental Method

The reduction experimental method is similar to the Pidgeon process. First, magnesite is calcined at 850°C and calcined magnesite powder is mixed with aluminum powder homogeneously. The mixture is pressed into pellets, and finally, the pellets are put into a reduction furnace. Reduction experiments were carried out in a horizontal pot (Fig. 1). The magnesia in the pellets was reduced by aluminum under the conditions of a vacuum and high temperature, magnesium was collected on a condenser, and reduction slag was left in a briquette bucket. After the completion of the reduction process, the reduction slag was removed from the reduction pot and then ground, briquetted, and sintered at a temperature up to 1800°C for 4–6 h in air. The reduction

rate of MgO ( $\eta_{\text{Mg}}$ ) was calculated by using Eq. 6, and the utilization rate of aluminum was calculated by using Eq. 7:

$$\eta_{\text{Mg}} = m_{\text{mg}}/M_{\text{Mg}} \times 100\% \quad (6)$$

$$r_{\text{Al}} = m_{\text{Al}}/M_{\text{Al}} \times 100\% \quad (7)$$

Here  $M_{\text{Mg}}$  is the initial quantity of magnesium in the raw materials,  $m_{\text{Mg}}$  is the quantity of magnesium on the condenser,  $m_{\text{Al}}$  is the quantity of aluminum that participated in the reduction reactions, and  $M_{\text{Al}}$  is the amount of added aluminum powder.

### PROCESS OF PRODUCING MAGNESIUM BY VACUUM ALUMINOTHERMIC REDUCTION USING MAGNESITE AS MATERIALS

In the process of producing magnesium via the vacuum aluminothermic reduction using magnesite as materials, if aluminum powder is added on the basis of Eq. 4, the maximum reduction rate of MgO is 75%, and the remaining MgO forms  $\text{MgO} \cdot \text{Al}_2\text{O}_3$ . In the reduction process, the reduction rate of MgO and utilization rate of reductant are the crucial criteria with which to judge the reduction performance. Both factors affect the ratio of raw materials to rough magnesium, the consumption of raw materials, and the cost of production.

#### Effect of the Reduction Temperature on the Reduction Rate of MgO

The reduction of MgO is an endothermic reaction, and therefore, the higher the reduction temperature, the faster the reduction rate, the shorter the time until a balanced state, and the higher the reduction rate of MgO in a given reaction time. However, the reduction temperature cannot exceed

1230°C (and is ideally lower than 1200°C) or the pot will withstand the temperature and the service life of the pot will rapidly shorten and the expense of repairs will increase sharply.

The effect of the reduction temperature on the reduction rate of MgO is shown in Fig. 2. Figure 2 shows that the initial temperature of the reduction reaction is lower than 950°C and that the reduction rate of MgO increases with a rise in the reduction temperature, but when the reduction temperature is higher than 1175°C, the reduction is close to completion. The reduction process is a little different from the Pidgeon process, whose initial temperature is higher than 1000°C and end temperature is about 1230°C. The temperature of the aluminothermic reduction is thus expected to be 50°C lower than that of the Pidgeon process, which is beneficial in terms of extending the service life of the reduction pot and saving energy.

#### Effect of Aluminum Addition on the Reduction Rate of MgO

The addition of aluminum powder also affects the reduction rate of MgO, and the reduction rate of MgO increases with an increase in aluminum addition. The effect of aluminum addition on the reduction rate of MgO is shown in Fig. 3. The figure reveals that the theoretical aluminum-additive amount, (i.e., the excess coefficient of aluminum) is 0% according to Eq. 4.

The reduction rate of MgO increases rapidly with an increase in aluminum addition, but the utilization rate of Al peaks at an excess coefficient of 5% and then reduces with an increase in the excess coefficient. The decrease in the utilization rate of Al undoubtedly increases the cost of the reduction process.

In the reduction process, the reaction is mainly described by Eq. 4 before the reduction rate of MgO reaches 75%, and when the reduction rate of MgO

Table I. Chemical composition of magnesite ore

Compound	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO
Content (%)	47.28	0.22	0.08	0.13	0.56

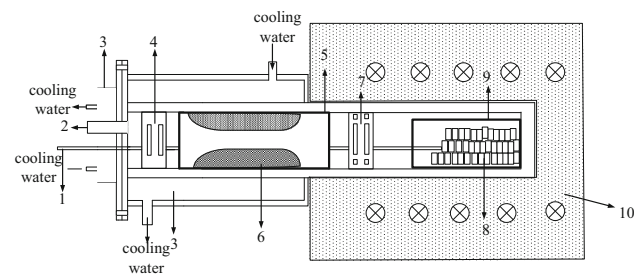


Fig. 1. Schematic drawing of the vacuum thermal reduction pot 1-thermocouple, 2-vacuum tube, 3-water-cooled jacket, 4-sodium and potassium condenser, 5-magnesium condenser, 6-rough magnesium, 7-thermal cutoff, 8-briquettes, 9-briquettes bucket, 10-furnace.

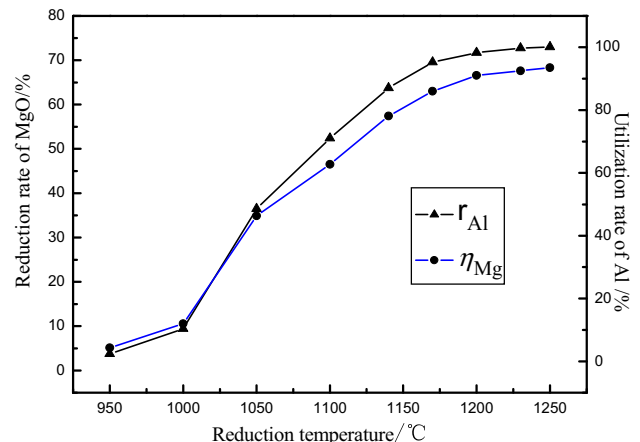


Fig. 2. Effect of the reduction temperature on the reduction rate of Mg and utilization rate of Al (reduction time of 2 h).

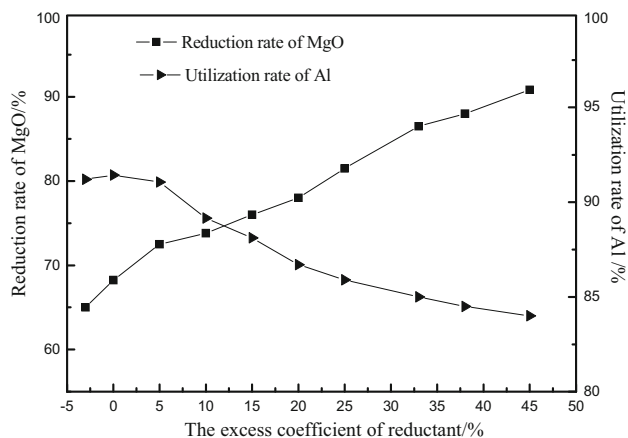


Fig. 3. Effect of the excess coefficient of Al on the reduction rate of MgO and utilization rate of Al (where the addition of aluminum is prescribed by Eq. 4, the reduction time is 2 h, and the reduction temperature is 1200°C).

reaches approximately 75%, the MgO remaining in the reduction material is almost entirely in the form of  $\text{MgO}\cdot\text{Al}_2\text{O}_3$ . If the dosage of aluminum addition further increases, MgO in the form of  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  can be partially reduced to metal magnesium and the reduction rate of MgO can exceed 90%. The reduction of MgO in  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  that is described by Eq. 5 has both positive and negative effects on the reduction process. On the one hand, it increases the reduction rate of MgO and decreases the ratio of raw material to rough magnesium and the consumption of materials, which further reduces energy consumption. On the other hand, the reduction of MgO in  $\text{MgO}\cdot\text{Al}_2\text{O}_3$  requires a higher reduction condition, which may reduce the utilization rate of Al and increase the consumption of Al, and lead to a higher cost of the reduction process. In addition, the content of MgO and  $\text{Al}_2\text{O}_3$  in the reduction slag is another issue to consider since the reduction slag will be sold as magnesium aluminate spinel. Above all, the addition of Al should be determined with comprehensive consideration of these effects to acquire the optimal benefit.

### Thermal Conductivity of Reduction Materials in the Reduction Process

Temperature is unquestionably a deciding factor of the reaction rate in both the aluminothermic process and the silicothermic process. A high temperature will lead to a higher reaction rate, shorter reaction time, and higher yield. In the reduction process, the temperature of materials in the reduction pot, especially at the center of the reduction pot, is closely related to the rate of heat transfer from the inside walls of the reduction pot. The heat transfer rate is also a main influencing factor of the reduction cycle, i.e., the time required to perform one reduction process. Heat transfer in the

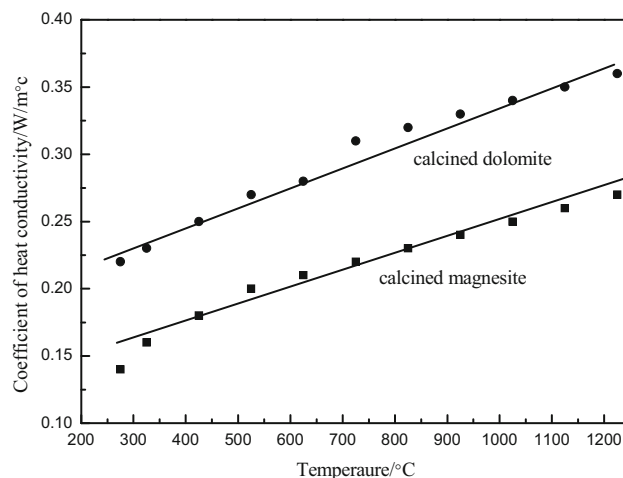


Fig. 4. Thermal conductivity of calcined magnesite and calcined dolomite.

reduction pot is based on heat conduction between materials, and it is aided by convection heat transfer of magnesium vapor and radiation heat transfer.

If we only consider raw materials, the thermal conductivity of calcined magnesite is lower than that of calcined dolomite (Fig. 4). In the Pidgeon process, the reduction materials consist of calcined dolomite (about 80 wt.%), ferrosilicon (about 17 wt.%), and fluorite (about 3 wt.%). All the reduction materials are solid at the reduction temperature, and the main form of heat transfer among reduction materials is thus heat conduction. In the aluminothermic process, although heat conduction is again the main form of heat transfer, the aluminum is a liquid at the reduction temperature, which benefits heat transfer. Additionally, with the reduction proceeding, the reduction rate of magnesium oxide will increase, the amount of metal reductant will decrease, more  $\text{Ca}_2\text{SiO}_4$  and  $\text{MgAl}_2\text{O}_4$  with low thermal conductivity will be produced, and the coefficients of heat conductivity of the Pidgeon process and aluminothermic process will decrease, but the coefficient of heat conductivity of the aluminothermic process will have a more gradual decline (Fig. 5).

The coefficient of heat conductivity in the aluminothermic process is initially lower than that in the Pidgeon process, but as the reaction proceeds, the relation reverses when the reduction rate of magnesium oxide exceeds 20%, and the coefficient of heat conductivity in the aluminothermic process is about twice that in the Pidgeon process when the reduction rate of magnesium oxide is 80%; the reduction reaction is close to completion at this point. Moreover, because of the lower starting reaction temperature, the higher reaction rate, and the greater magnesium vapor production (where the production of magnesium vapor is about 1.8 times that in the Pidgeon process),<sup>16</sup> the coefficient of convective heat transfer in the

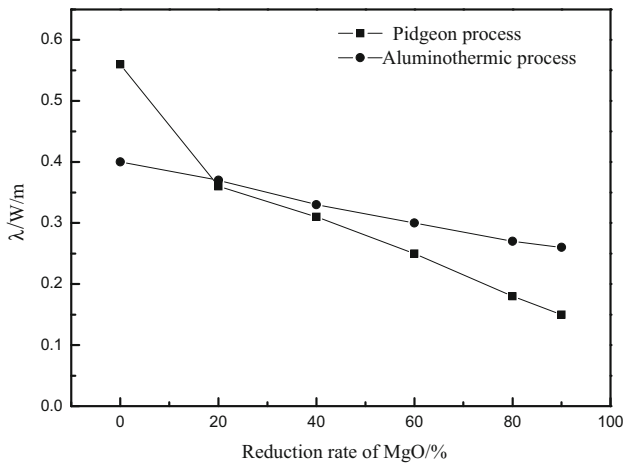


Fig. 5. Thermal conductivity of the reduction slag in the aluminothermic process and Pidgeon process (1200°C).

**Table II. Main constituents of the reduction slag**

Compound	MgO	Al <sub>2</sub> O <sub>3</sub>	CaO	SiO <sub>2</sub>	Al	Fe <sub>2</sub> O <sub>3</sub>
Content (%)	26–28	64–67	1.0–1.5	0.4–0.7	1.0–2.0	<0.5

aluminothermic process will be higher than that in the Pidgeon process, which is also favorable for heat transfer. All the above are beneficial in terms of reducing the reduction cycle of the aluminothermic process, and preliminary industrial experiments showed that the reduction rates at 8 and 10 h were similar while those at 8 and 10 h in the Pidgeon process differed by more than 5%. This shows that the reduction time of the aluminothermic process can be reduced by at least 2 h.

### Phase and Microstructure of the Reduction Slag

Pure magnesium metal can be obtained by remelting and refining rough magnesium. For the case that the addition of calcined magnesite and aluminum powder is based on Eq. 4, the main composition of the reduction slag is listed in Table II and the x-ray diffraction (XRD) analysis is presented in Fig. 6. According to the analysis of the diffractogram and composition of the reduction slag, there was approximately 93% MgAl<sub>2</sub>O<sub>4</sub>, 3% MgO, 1% of unreacted aluminum metal, and 2% other ingredients, namely, CaO, SiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>.

The microstructure of the reduction slag is shown in Fig. 7. MgAl<sub>2</sub>O<sub>4</sub> in the reduction slag is mainly in the form of small dense grains. Because of the escape of magnesium vapor and volume shrinkage of MgAl<sub>2</sub>O<sub>4</sub>, the porosity of the reduction slag is high.

## PROCESS OF PRODUCING MAGNESIUM ALUMINATE SPINEL BY USING REDUCTION SLAG AS MATERIALS

Magnesium aluminate spinel (MgAl<sub>2</sub>O<sub>4</sub>, MA spinel), consisting of 28.2% MgO and 71.8% Al<sub>2</sub>O<sub>3</sub> in theory, has useful physical, chemical, and thermal properties, at both normal and elevated temperatures.<sup>16,17</sup> Because of its high melting point (2135°C), lower average coefficient of linear expansion, and high resistance to attack by most of the acids and alkalis, the MA spinel has been widely used in the structural, chemical, optical, and electrical industries, and it has especially been used as a refractory material.<sup>18,19</sup>

The conventional method of synthesizing industrial MA spinel is a sintering process that involves a solid-state reaction.<sup>20</sup> The method uses pure alumina and magnesite as materials and comprises three main steps. The first step is the calcination of magnesite to obtain MgO. The second step is a briquetting process. In the second step, calcined magnesite and pure Al<sub>2</sub>O<sub>3</sub> are mixed in exact proportions and then pressed into pellets. The third step is a sintering process. The sintering of refractory MA spinel is a solid-state reaction, and since the synthesis of MA spinel from calcined magnesite and Al<sub>2</sub>O<sub>3</sub> powders at high temperature is accompanied by a 7% to 8% volume expansion, the sintering process always involves two calcination stages.<sup>21,22</sup> The first is the precalcination stage of the oxides in a lower temperature range (1100°C to 1300°C) that allows 55% to 70% spinellization. The second is a high-temperature sintering stage. In the second stage, the reactive MA spinel obtained in the first stage is repulverized, ground, and briquetted into pellets. The pellets are sintered in a rotary kiln under the conditions of a highest temperature of 1700°C to 1800°C, and the sintering time exceeds 30 h to achieve a dense bulk with desired properties. Since the conventional method needs to repeat calcinations stages and requires a long sintering time, it has high energy consumption.

There is a small amount of unreacted metal aluminum and unreacted MgO, but more than 93% of the reduction slag obtained after the aluminothermic reduction is MgAl<sub>2</sub>O<sub>4</sub>. It is possible to omit the stage of precalcination of the oxides and go straight to the high-temperature sintering stage using the reduction slag as a material to produce refractory MA spinel. When the reduction slag is calcined at a higher temperature of 1600°C to 1800°C, the volume of MgAl<sub>2</sub>O<sub>4</sub> in the reduction slag can be further reduced and the density of the reduction slag increased appreciably, while all the aluminum powder that did not react will become alumina and react with MgO to form MgAl<sub>2</sub>O<sub>4</sub>. A pure and high-density MA spinel can thus be obtained. Compared with the traditional method, the proposed method of using reduction slag as material to produce refractory MA spinel is an advanced technique having a low cost, a short process, and low energy consumption.

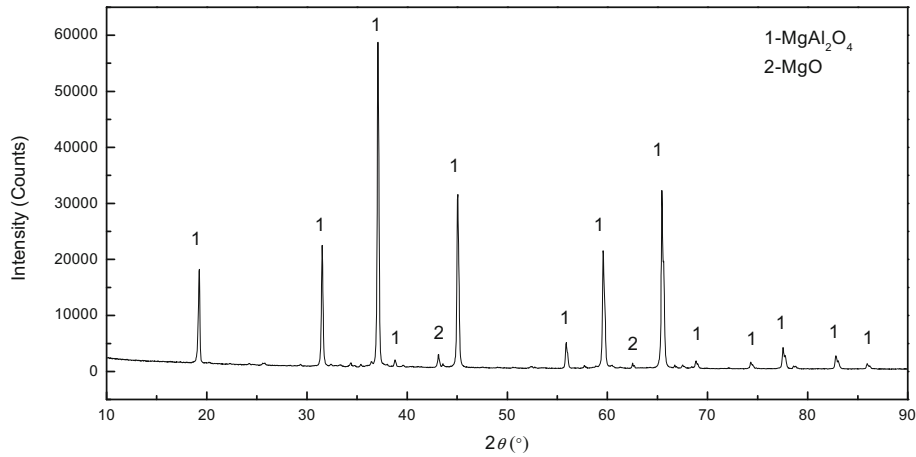


Fig. 6. XRD analysis of the reduction slag.

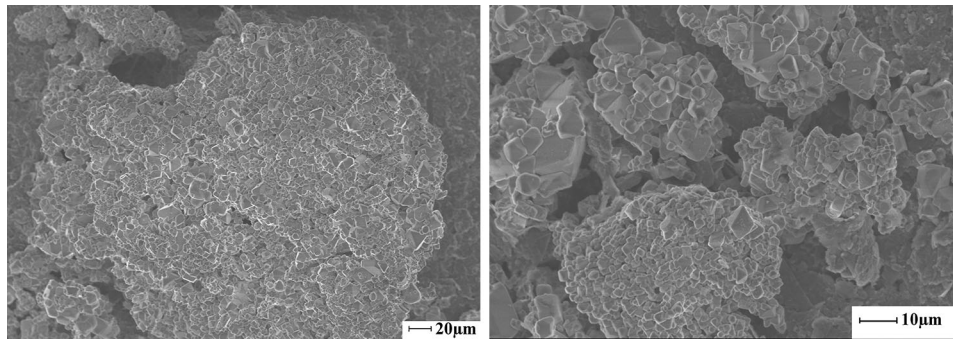


Fig. 7. Scanning electron microscopy of the reduction slag.

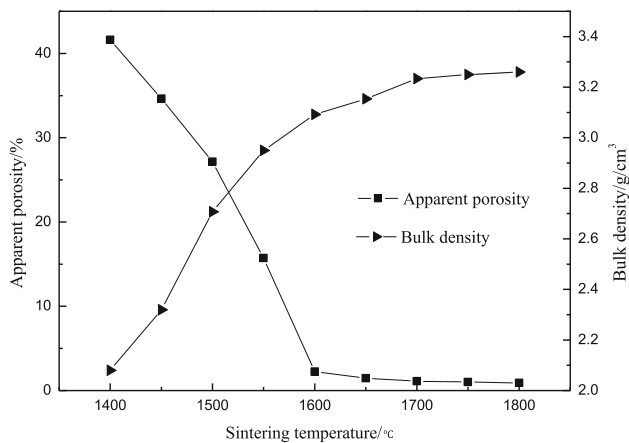


Fig. 8. Effect of the sintering temperature on the apparent porosity and bulk density of samples (4-h duration).

### Effect of the Sintering Temperature on the Bulk Density of MA Spinel

The bulk density of MA spinel is mainly affected by the sintering temperature. Figure 8 shows the density and apparent porosity variation of samples at various temperatures.

Figure 8 shows that the densities of samples greatly improve with an increase in sintering temperature from 1400°C to 1700°C (viz. 2.10 g/cm<sup>3</sup> to 3.204 g/cm<sup>3</sup>). The variation trends of the apparent porosity of samples are similar, with the apparent porosity reducing from 41.62% to 1.22% with increasing calcination temperature. When the calcination temperature was 1800°C, the density and apparent porosity of a sample are 3.24 g/cm<sup>3</sup> and 1.01%, respectively.

### Phase Analysis of MA Spinel

The XRD signatures of the MA spinel produced using reduction slag as material and calcined at 1800°C for 4 h are presented in Fig. 9. A comparison with standard cards shows that all major diffraction peaks belong to MgAl<sub>2</sub>O<sub>4</sub> while CaAl<sub>12</sub>O<sub>19</sub> is present as a minor phase. The XRD results of industrial MA spinel produced employing the conventional synthesis method are displayed in Fig. 10.

Figure 9 shows that the only other phase detected within the detection limits of XRD analysis is CaAl<sub>12</sub>O<sub>19</sub>, MgO, SiO<sub>2</sub>, and aluminum metal could not be found even in trace amounts. A comparison of Figs. 9 and 10 reveals similar XRD patterns, with the only difference being that the characteristic

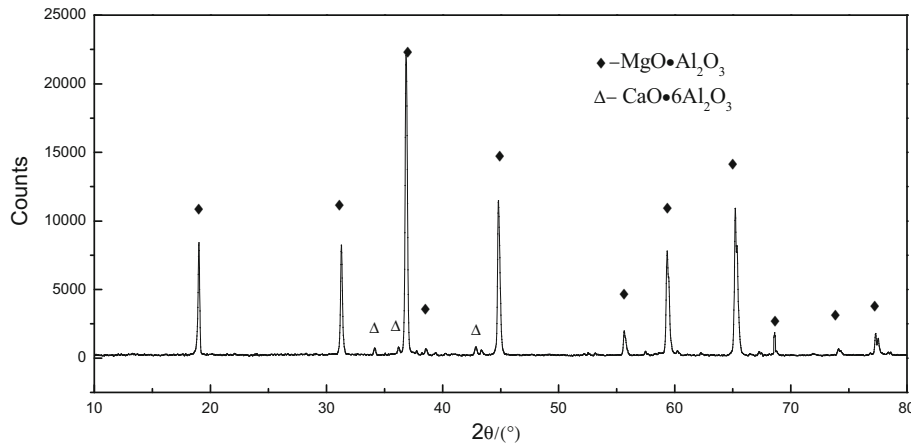


Fig. 9. XRD analysis of MA spinel produced using reduction slag as material.

peaks belonging to  $\text{CaAl}_{12}\text{O}_{19}$  in Fig. 9 are higher than those in Fig. 10. It may thus be concluded that the content of  $\text{CaAl}_{12}\text{O}_{19}$  in MA spinel produced using aluminothermic reduction slag as material is higher than that in MA spinel produced using the conventional method.

The morphological features of MA spinel powder calcined at  $1800^\circ\text{C}$  for 4 h are shown in Fig. 11, and the energy-dispersive x-ray spectroscopy (EDS) analysis is presented in Fig. 12.

Figure 11 shows that the microstructure of MA spinel is compact and that there are no pores. The powder is all  $\text{MgAl}_2\text{O}_4$ , and no other crystals, such as periclase or corundum, are observed.

Under appropriate technological conditions, the bulk density of MA spinel exceeds  $3.24\text{ g/cm}^3$  and the apparent porosity is lower than 1%. The product consisting of 26% to 28%  $\text{MgO}$ , 72% to 74%  $\text{Al}_2\text{O}_3$ , and about 0.7%  $\text{SiO}_2$  conforms to industry standard.

### COMPARISON OF THE ALUMINOTHERMIC REDUCTION PROCESS AND PIDGEON PROCESS

According to the above-mentioned experimental results, the performance of the main techniques of the aluminothermic reduction process can be obtained. Figure 13 presents the flowchart and material balance. Table III compares the technique performance comparison of the Pidgeon process and aluminothermic reduction process.

Table III shows that the aluminothermic reduction process has many advantages over the Pidgeon process.

- (1) The consumption of raw materials is 50% less and the energy consumption of calcination is more than 70% less in the aluminothermic reduction process.
- (2) The ratio of raw materials to rough magnesium in the reduction process of the aluminothermic reduction process is 3.2–3.4:1, which is about half of that in the Pidgeon

process. This indicates that the energy consumption is more than 50% less and the productivity double in the aluminothermic reduction process.

- (3) The aluminothermic reduction is carried out at a lower temperature, which is beneficial in terms of extending the service life of the reduction pot and reducing the expenses of repairs. In addition, the high heat transfer coefficient and reaction rate of the aluminothermic reduction shorten the reduction time and thus save energy.
- (4) The reduction slag of the aluminothermic reduction can be used to produce value-added refractory MA spinel and to eliminate residue discharge.

Overall, compared with the Pidgeon process, the aluminothermic reduction process of magnesium production can save materials by as much as 50%, increase productivity up to 100%, and save energy by more than 50%. It can also reduce  $\text{CO}_2$  emission up to 60% and realize zero discharge of waste residue.

### CONCLUSION AND DISCUSSION

From a comparison of benefits of magnesium smelting employing the aluminothermic reduction process and the Pidgeon process, it is concluded that magnesium production by vacuum aluminothermic reduction with magnesium aluminate spinel as a by-product is an energy-saving and environmentally friendly method.

The initial reaction taking place in the aluminothermic reduction process by using magnesite as material is  $4\text{MgO}(\text{s}) + 2\text{Al}(\text{l}) = 3\text{Mg}(\text{g}) + \text{MgO} \cdot \text{Al}_2\text{O}_3(\text{s})$ , however the reaction is  $(4a + b)\text{MgO}(\text{s}) + 2a\text{Al}(\text{l}) = 3a\text{Mg}(\text{g}) + a\text{MgO} \cdot \text{Al}_2\text{O}_3(\text{s}) + b\text{MgO}(\text{s})$  when aluminum is deficient and  $(4c + 3d)\text{MgO}(\text{s}) + (2c + 2d)\text{Al}(\text{l}) \rightarrow (3c + 3d)\text{Mg}(\text{g}) + c\text{MgO} \cdot \text{Al}_2\text{O}_3(\text{s}) + d\text{Al}_2\text{O}_3$  when aluminum is sufficient. The former reaction is easier, while the latter

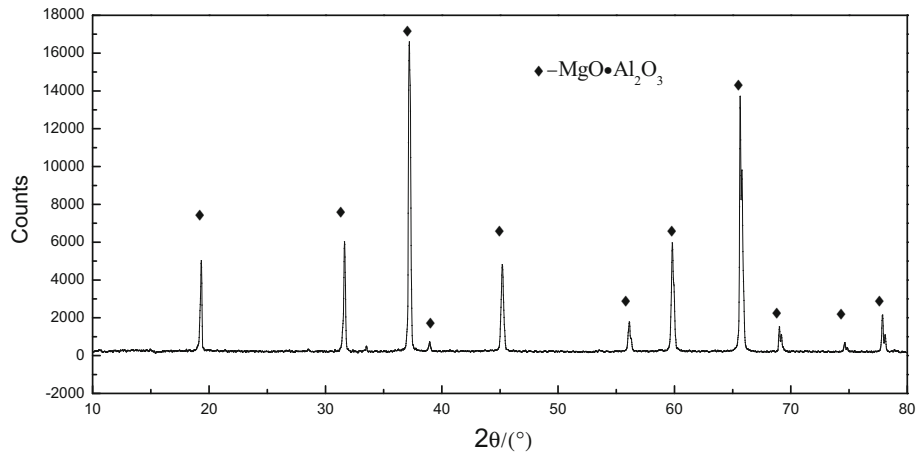


Fig. 10. XRD analysis of MA spinel purchased from Haicheng Huayin Group Company, China, and produced employing the conventional synthesis method.

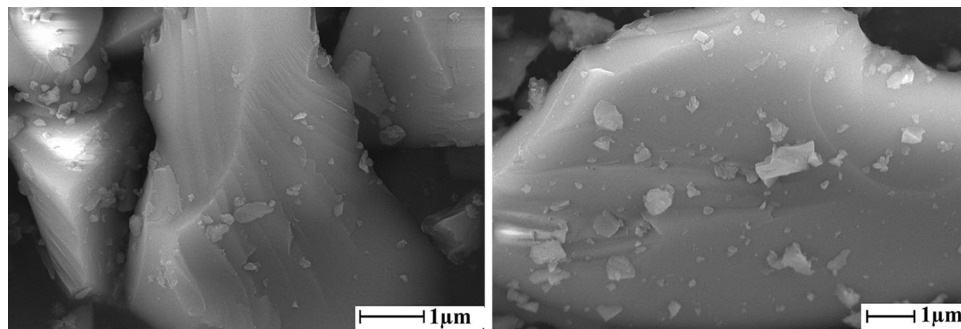


Fig. 11. Scanning electron microscopy of MA spinel power synthesized at 1800°C for 4 h.

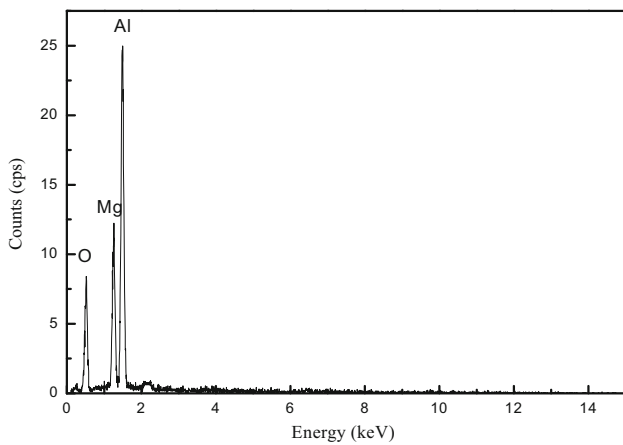


Fig. 12. EDS analysis of MA spinel power synthesized at 1800°C for 4 h.

requires higher temperatures and a greater coefficient of excess aluminum, but both achieve good results under the same conditions of the Pidgeon process. All MA spinel products with 40% to 95%  $Al_2O_3$  can be obtained by adjusting the value of a, b, c, and d.

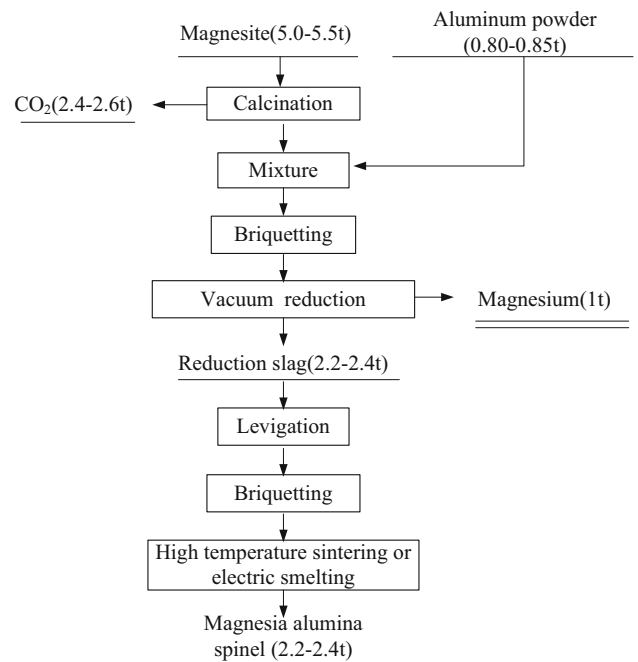


Fig. 13. Flowchart of the aluminothermic reduction process.



**Table III. Comparison of the performance of the technique of the pigeon process and aluminothermic reduction process (per ton magnesium)**

Project	Pidgeon process	Aluminothermic reduction process
Material consumption	Dolomite 10.5–11t	Magnesite 5.0–5.5t
Calcination temperature	1150°C–1200°C	800°C–850°C
Reductant consumption	ferrosilicon 1.05–1.1t	aluminum powder 0.80–0.85t
Fluorite	0.2	0
Reduction temperature	1200°C–1230°C	1170°C–1200°C
Ratio of raw materials to rough magnesium	6.0–6.5	3.2–3.4
Reduction slag	5.0–5.5	2.2–2.4
By-production	0	2.2–2.4 MA spinel
Waste residue	5.0–5.5	0
CO <sub>2</sub> emission	>30	<15
Energy consumption	5–6t tce	2.5–3.0t tce

A drawback to the aluminothermic reduction process is that the content of impurities in MA spinel produced using aluminothermic reduction slag as material is higher than that in MA spinel produced employing the conventional method. The impurities mainly come from magnesite. It takes about 1.5–2.5 tons of magnesite to produce one ton of reduction slag, and the majority of impurities remains in the reduction slag and will remain in the MA spinel except for a small amount of impurities that enters the metal magnesium, while it takes only about 0.6 tons of magnesite to produce one ton of MA spinel employing the conventional method. The content of impurities of MA spinel will thus be two to three times that for the conventional method, and the main impurities of magnesite are CaO, SiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>. The impurities, especially SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>, strongly affect the densification and properties of spinel, and the content of SiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> in MA spinel will thus be less than 1% in general. The CaO in reduction slag will react with Al<sub>2</sub>O<sub>3</sub> to form calcium hexaaluminate (CaAl<sub>12</sub>O<sub>19</sub> or CaO·6Al<sub>2</sub>O<sub>3</sub>) in the high-temperature sintering stage.<sup>23</sup> Calcium hexaaluminate, which is a new high-temperature, corrosive-resistant material, can increase the strength of MA spinel when its sheets are interspersed in spinel.<sup>24,25</sup>

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