

## MAGNESIUM PRODUCTION BY VACUUM ALUMINOTHERMIC REDUCTION OF A MIXTURE OF CALCINED DOLOMITE AND CALCINED MAGNESITE

Wen-xin Hu, Nai-xiang Feng, Yao-wu Wang, Zhi-hui Wang

School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning 110004, China

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### Abstract

A new method of magnesium production was proposed that using a mixture of calcined dolomite and calcined magnesite as raw materials with the molar ratio of MgO to CaO was 6:1 by vacuum aluminothermic reduction. The reduction process was studied by thermodynamic analysis and X-ray diffraction analysis of reduction residue. The reaction of reduction process was  $\text{CaO} + 6\text{MgO} + 4\text{Al} = \text{CaO}\cdot 2\text{Al}_2\text{O}_3 + 6\text{Mg}$ . The effect of briquetting pressure, reduction temperature, time and  $\text{CaF}_2$  ( $\text{MgF}_2$ ) on reduction ratio of MgO was investigated. And the reduction residue that the main phase of  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  was leached in alkaline solution for producing sodium aluminate—the raw material for special alumina. The results show that the reduction ratio is increased with increasing of the temperature, time, briquetting pressure in range from 40 to 100 MPa and addition of  $\text{CaF}_2$  or  $\text{MgF}_2$  in range from 0 to 3%. The alumina leaching ratio of reduction residue reached 88% at the conditions of leaching temperature 95 °C and the concentration ratio of  $\text{Na}_2\text{CO}_3$  to NaOH was 100:75 in leaching solution.

### Introduction

Magnesium is the lightest metal of the commonly used metals and can be applied widely. For example, there are metallurgical applications, chemical applications, structural applications, and automobile parts production [1,2]. It means huge demands for magnesium in the world. The raw materials of magnesium production such as magnesite and dolomite are widespread and high purity magnesium can be produced under low cost, simple and flexible conditions of vacuum thermal reduction process versus electrolytic production.

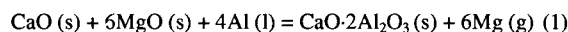
The Pidgeon process is a widely used process in vacuum thermal reduction process, and this technology has been in stage of maturity [3-5]. But because of the low reactivity of ferrosilicon alloy, higher reduction temperature (>1170 °C) and longer reduction time (>7 hours) are required, which in order to reach high reduction ratio of MgO. The reduction ratio of MgO was only 73.9% at the conditions of temperature 1443 K, time 120 min [6]. More energy is needed for heating, the service life of Ni-Cr alloy reactors decrease greatly under vacuum and the conditions mentioned above, make higher cost of the Pidgeon process eventually; the residue after reduction (main phase is  $\gamma\text{-}2\text{CaO}\cdot\text{SiO}_2$ ) is useless to other fields, such as cement industry with a reason that unreacted MgO has negative influence on the performance of cement [7,8]. According to the above information, there are two problems should be solved, firstly, the service life of reactors and the high cost of process; secondly, the emission of  $\text{CO}_2$  and the waste of reduction residue.

A new vacuum thermal reduction method is proposed for solving the two problems about the Pidgeon process in the present paper. The new reduction process is aluminothermic reduction of a mixture of calcined dolomite and calcined magnesite with the molar ratio of MgO to CaO was 6:1. It is studied by thermodynamic analysis and the effects of

reduction temperature, reduction time, vacuum of reduction system, briquetting pressure and addition of  $\text{CaF}_2$  or  $\text{MgF}_2$  on the reduction ratio of MgO, which for ensuring the optimal conditions of reduction process. Using alkaline solution to leach alumina from  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$ , the main phase of reduction residue. The new magnesium production method in the present paper is in order to create a green, lower cost but higher economic benefit process.

### Thermodynamic Analysis

Figure 1 is the X-ray diffraction analysis of reduction residue, the reduction condition of experiment is reduction temperature 1413 K, reduction time 120 min, pellets forming pressure of 50 MPa and vacuum of 4 Pa. It is noticed that  $\text{CaO}\cdot 2\text{Al}_2\text{O}_3$  phase with higher intensity; the other phases are from raw materials. Thus, the main reaction of reduction process occurred in reduction is



$$\Delta G^\circ = 1013.7 - 0.615T \quad (\text{kJ/mol}) \quad (2)$$

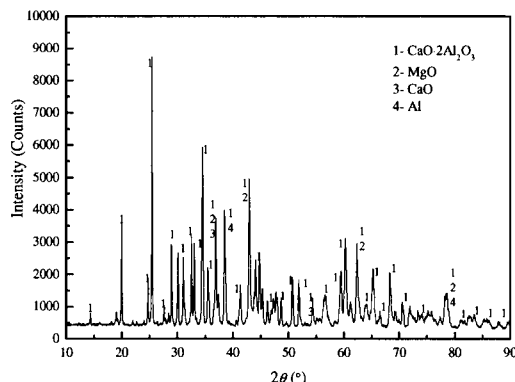


Figure 1. The XRD pattern of reduction residue.

The relationship between the equilibrium magnesium partial pressure ( $P_{\text{Mg}}$ ) and reduction temperature is given by Equation 3.

$$\Delta G = 1013.7 - 0.615T + RT \ln \left[ \frac{(P_{\text{Mg}}/P^\circ)^6}{(\alpha_{\text{Al}}/a^\circ)^4} \right] \quad (\text{kJ/mol}) \quad (3)$$

Where  $\alpha_{\text{Al}}$  is the activity of aluminum;  $a^\circ$  and  $P^\circ$  are values of standard state;  $R$  is the gas constant.

The equilibrium temperature of Equation 1 is 1648.3 K at reduction system pressure of 1 atm. But the reaction temperature decreases to 904.4 K at the experimental vacuum of 4 Pa. Therefore, the reaction Equation 1 could occur at temperatures of 1223, 1273, 1323, 1373, 1413, 1443 and 1473 K at vacuum of 4 Pa (during the reduction process,  $P_{\text{Mg}}$  is approximately equal to the pressure of vacuum reduction system [9], which displays on vacuumometer).

## Experimental

### Materials

Dolomite and magnesite were obtained from Liaoning, China; aluminum powder (purity 99%), CaF<sub>2</sub>, MgF<sub>2</sub>, NaOH and Na<sub>2</sub>CO<sub>3</sub> were supplied by Tian Jin Kernal Chemical Reagent CO., LTD. Table I and II show the chemical compositions of dolomite and magnesite using chemical analysis.

Table I. Chemical composition of dolomite.

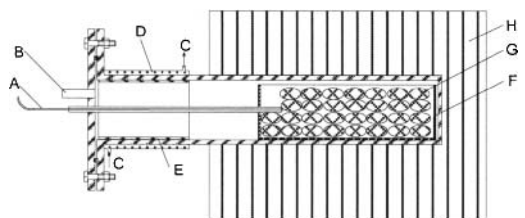
Component	MgO	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Content (% , ω)	23.62	29.86	0.22	0.10

Table II. Chemical composition of magnesite.

Component	MgO	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Content (% , ω)	47.34	0.67	0.13	0.08

### Apparatus

Figure 2 schematically shows the experimental apparatus for reduction. A furnace using silicon carbide rods was used to heat the reactor which was made of high-temperature alloyed steel; temperature control system was used to control the heating ratio of reduction system and shown the temperature which was measured by NiCr-NiSi thermocouple; vacuum system was made up of ZJP-70 roots vacuum pump and ZX-15 rotary-vane vacuum pump; condenser, the upper part of reactor was used to condense magnesium vapor and collected magnesium.



A- thermocouple  
B- vacuum tube  
C- circulating water  
D- water-cooled jacket  
E- condenser  
F- briquettes bucket  
G- briquettes  
H- furnace

Figure 2. Schematic of experimental apparatus.

### Procedures

The vacuum thermal reduction experiments were carried out by using a mixture of calcined dolomite and calcined magnesite. According to the experimental data of calcinations, dolomite and magnesite should be calcined at 1060 °C and 830 °C for 90 min respectively for ensuring the reactivity of MgO-CaO and MgO. The calcined dolomite and calcined magnesite were pulverized and sieved 150~180 μm out, mixed with the molar ratio of MgO, CaO to Al 6:1:4. The mixed charges were formed into pellets under different pressure, having a diameter of 25 mm and a thickness of about 10 mm. The pellets were charged into the reactor for reduction experiments. The magnesium was reduced by aluminum in the conditions of vacuum and high temperature. The magnesium was collected on the condenser. The reduction residue was

leached under the conditions of leaching temperature 95 °C and the concentration ratio of Na<sub>2</sub>CO<sub>3</sub> to NaOH was 100:75 by calculation of Equation 6. The flow sheet of process show is shown in Figure 3. After reduction and reactor cooling, the condensed magnesium product and the residue obtained were weighed and analyzed.

The reduction ratio of MgO (*R*) is calculated by the following formula:

$$R = \frac{m_r}{m_0} \times 100\% \quad (4)$$

Where *m*<sub>0</sub> is the initial quantity of magnesium in the raw materials and *m*<sub>r</sub> is the quantity of magnesium on condenser.

The leaching ratio of Al<sub>2</sub>O<sub>3</sub> according to the following formula:

$$\eta_{Al_2O_3} = \frac{\omega_l}{\omega_0} \times 100\% \quad (5)$$

Where *ω*<sub>0</sub> is the quantity of Al<sub>2</sub>O<sub>3</sub> (elemental aluminum in reduction residue is convert to Al<sub>2</sub>O<sub>3</sub>), *ω*<sub>l</sub> is the quantity of Al<sub>2</sub>O<sub>3</sub> in leaching solution.

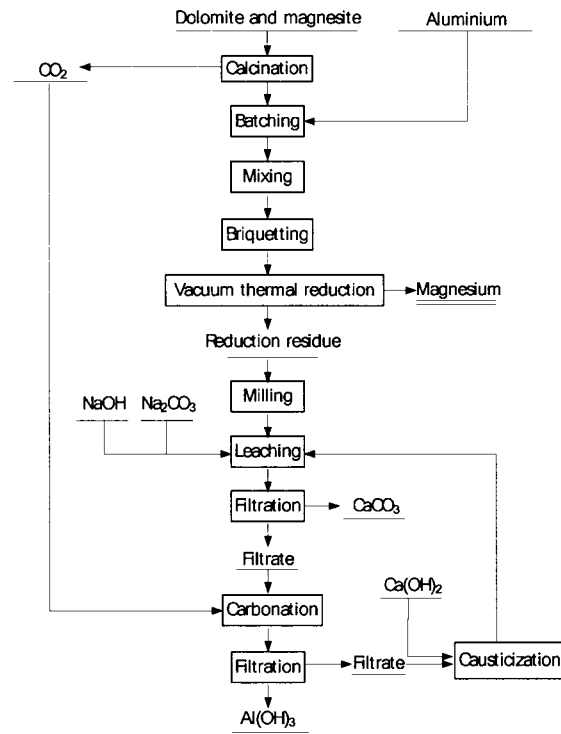


Figure 3. The flow sheet of reduction and leaching process.

### Analysis of Experimental Results

#### Effect of Reduction Temperature on Reduction Ratio of MgO

Figure 4 shows the changes in reduction ratio of MgO at different temperatures. At the conditions of briquetting pressure of 50 MPa, reduction time 120 min and vacuum 4 Pa. With increasing temperature from 1223 K to 1413 K, the reduction ratio of MgO increased remarkably, from 44.47% to 82.06%. The reduction ratio of MgO increased slowly at

temperature range from 1413 K to 1443 K. The final reduction ratio was 91.35% at 1473 K.

Reduction temperature is an important factor to the reaction rate; the reaction ratio was accelerated with temperature increasing. But at the stage of 1443 K, the reduction is close to the end which the reason of reduction ratio increased slowly. The high reaction rate and good results of reduction ratio of MgO needed high temperature. But the reasonable reduction temperature is chosen 1413 K by experimental data. The reason that decreasing the reduction temperature for saving cost of high-temperature alloy is one of the principal objectives of the present reduction process. At 1413K, the reduction ratio of MgO is higher than Pidgeon process at 1473 K [6]. The reduction ratio of MgO should increase by change other factors, such as reduction time.

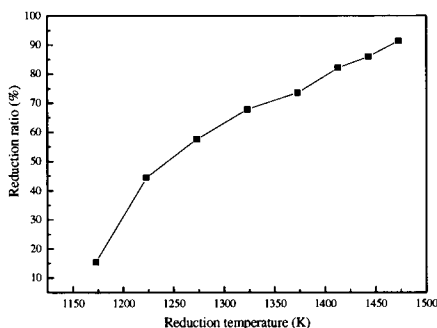


Figure 4. Effect of reduction temperature on reduction ratio of MgO.

#### Effect of Reduction Time on Reduction Ratio of MgO

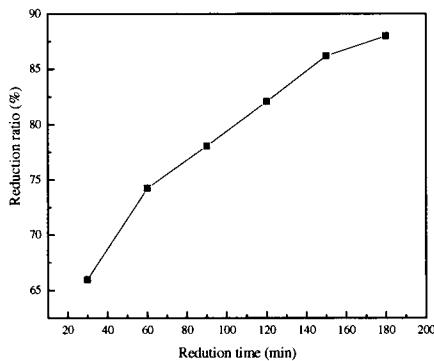


Figure 5. Effect of reduction time on reduction ratio of MgO (the initial reduction ratios according to experimental data are 40.9% in temperature-rise period from room-temperature to 1413 K).

The effect of reduction time on reduction ratio of MgO is presented in Figure 5. The reduction temperature was 1413 K, briquetting pressure 50 MPa and vacuum 4 Pa. The reduction ratio increased obviously at the initial reaction stage from 30 min to 150 min, the reduction ratio reached 86.18% at 150 min. After reduction time of 150 min, the reduction ratio of MgO increased slowly that only increasing 1.81% at 180 min. The reduction ratio increased almost no more. It should be the meaning of the end of reduction.

The more energy will lead to high reaction rate of reduction process. The energy which was supported to pellets by heat transfer from furnace to pellets by thermal radiation almost,

and then from surface into the core of pellets with reduction time extended. In present paper, time of 150 min was not the best reduction time, but the time which the corresponding reduction ratio of MgO was closed to the maximum. It is one of key links for saving the cost of energy, and enhanced the effects of briquetting pressure and addition of CaF<sub>2</sub> or MgF<sub>2</sub> on reduction ratio of MgO.

#### Effect of Briquetting Pressure on Reduction Ratio of MgO

Figure 6 shows the effect of briquetting pressure on reduction ratio of MgO. The reduction temperature was 1413 K, reduction time 120 min and vacuum 4 Pa. For the briquetting pressure of 100 MPa, the reduction ratio proceeded the fastest and the reduction ratio was 88.96%. For the briquetting pressure of 50 MPa or 200 MPa, the reduction ratio was decreased remarkably. The reason of this phenomenon is from 50 MPa to 100 MPa, increasing briquetting pressure can increase the contact area between MgO-CaO and reduction agent; from 100 MPa to 200 MPa, the briquetting pressure make the gap is too small between MgO-CaO and reduction agent that magnesium vapor is difficult to escape from the pellets. Thus the appropriate briquetting pressure could balance progresses of contact between MgO-CaO and reduction agent, and the escape of magnesium vapor.

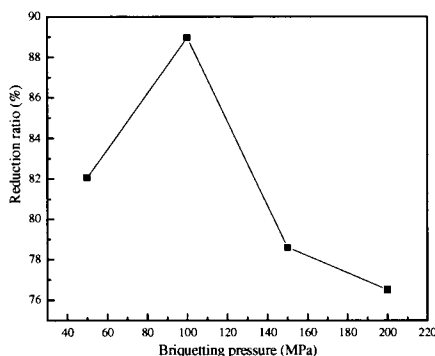


Figure 6. Effect of briquetting pressure on reduction ratio of MgO.

#### Effect of CaF<sub>2</sub> or MgF<sub>2</sub> on Reduction Ratio of MgO

Figure 7 illustrates the effect of CaF<sub>2</sub> or MgF<sub>2</sub> on reduction ratio of MgO. The reduction temperature 1413 K, briquetting pressure 50 MPa and vacuum 4 Pa. At the addition of CaF<sub>2</sub> and MgF<sub>2</sub> 1% of total charge mass respectively, the reduction rates were 87.07% and 84.97%. The reduction rates reached the maximum at the addition of CaF<sub>2</sub> (MgF<sub>2</sub>) 3%. With the additions of MgF<sub>2</sub> 5%, the reduction rates slightly decreased that 95.59% and 94.95%. The addition of CaF<sub>2</sub> (MgF<sub>2</sub>) could activate the surface of MgO-CaO and the reactivity of oxygen ion was increased which enhanced the reaction between MgO-CaO and aluminum.

The addition of CaF<sub>2</sub> (MgF<sub>2</sub>) was an effective way to accelerate reduction progress, but the mass of addition should be appropriate as 3% of total charge mass according to the considerate of cost and the high reduction ratio of magnesium. The accelerating effect of MgF<sub>2</sub> to reduction was better than CaF<sub>2</sub> of addition of 3% or above.

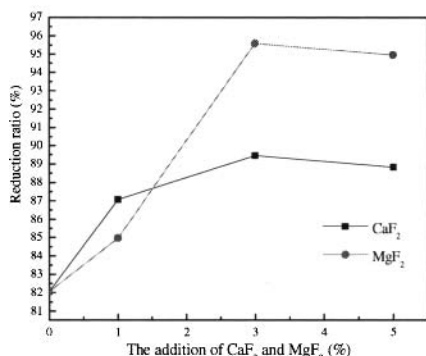


Figure 7. Effect of the addition of CaF<sub>2</sub> or MgF<sub>2</sub> on reduction ratio of MgO.

The reduction ratio of MgO was 97.01% at temperature 1413 K, time 150 min, briquetting pressure 100 MPa and 3% MgF<sub>2</sub>. The magnesium produced in reduction as shown in Figure 8, the ratio of purity beyond 99.17% by chemical analysis.

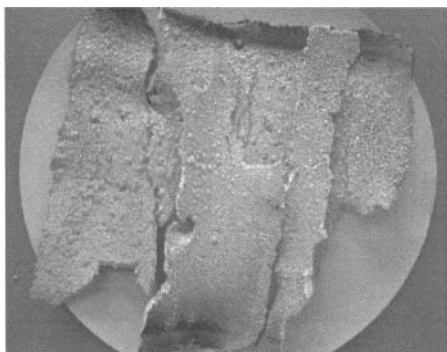
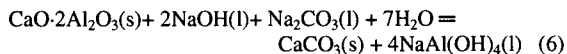


Figure 8. The magnesium produced in reduction.

#### Alumina Leaching from Reduction Residue

According to the XRD pattern shown in Figure 1, CaO·2Al<sub>2</sub>O<sub>3</sub> was the major phase in reduction residue. Using alkaline solution of a mixture of Na<sub>2</sub>CO<sub>3</sub> and NaOH with the concentration ratio of 100:75 to leach NaAl(OH)<sub>4</sub> from CaO·2Al<sub>2</sub>O<sub>3</sub> at temperature 95 °C and time 120 min. The leaching ratio of Al<sub>2</sub>O<sub>3</sub> reached 88%. NaAl(OH)<sub>4</sub> was converted to Al(OH)<sub>3</sub> by carbonation. CO<sub>2</sub> was collected at the stage of dolomite and magnesite calcinations. This step is contributed to reduce cost and reduced the emission of CO<sub>2</sub>. The product of Al(OH)<sub>3</sub> is shown in Figure 9.

The phase of residue after leaching was shown in Figure 10. CaCO<sub>3</sub> could be isolated firstly and then be the raw material of CaO in cement industry. The leaching process is the following



and the reaction during the carbonation of NaAl(OH)<sub>4</sub> is

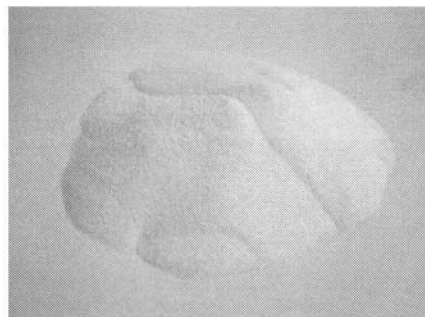


Figure 9. The product of Al(OH)<sub>3</sub>.

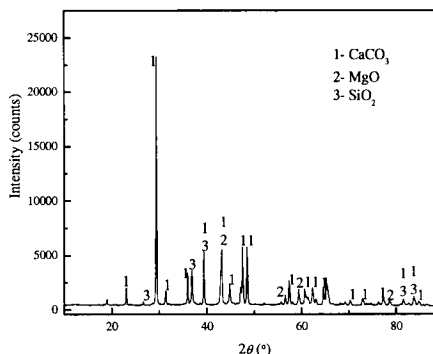


Figure 10. The XRD pattern of leaching residue.

#### Conclusions

- (1) The reduction temperature, reduction time, briquetting pressure and the addition of CaF<sub>2</sub> (MgF<sub>2</sub>) are important factors to reduction process. With increasing the above factors increased the reduction ratio of MgO. But briquetting pressure and the addition of CaF<sub>2</sub> (MgF<sub>2</sub>) should be in the optimum ranges.
- (2) According to the analysis of experimental results, the possible industrial operating conditions of reduction process are reduction temperature 1413 K, reduction time 150 min, vacuum 4 Pa, pressure for briquetting of raw materials 100 MPa and the addition of 3% MgF<sub>2</sub>.
- (3) The main phase of reduction residue is CaO·2Al<sub>2</sub>O<sub>3</sub> that can extract sodium aluminate and produce Al(OH)<sub>3</sub> by carbonation. The leaching ratio reached 88% under leaching temperature 95 °C of 120 min and the concentration ratio of Na<sub>2</sub>CO<sub>3</sub> to NaOH was 100:75.
- (4) Compare to the Pidgeon process, the new reduction technology presents in this paper can accelerate reduction process, Al(OH)<sub>3</sub> can be produced from reduction residue, CO<sub>2</sub> is collected at the stage of dolomite and magnesite calcinations and CaCO<sub>3</sub> in the leaching residue also can be used, which mean the new reduction technology reduce production cost effectively and almost none waste be discharged into environment.

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