Magnesium Technology 2012
Edited by: Suveen N. Mathaudhu, Wim H. Sillekens, Neale R. Neelameggham, and Norbert Hort
TMS (The Minerals, Metals & Materials Society), 2012

EXPERIMENTAL STUDY ON MAGNESIUM EXTRACTED FROM ASCHARITE MINERAL BY ALUMINIUM

Peng Jianping[1], Wu Xiaolei[1], Feng Naixiang[1], Zhou Shigang[1], Di Yuezhong[1]
[1]School of Materials and Metallurgy, Northeastern University, Shenyang, 110819, China

Keywords: ascharite mineral, magnesium, aluminum powder, vacuum thermal reduction

Abstract

In order to effectively utilize the ascharite mineral, in Liaoning province of China, the paper studied to extract magnesium from ascharite mineral with aluminum powder as reductant by vacuum thermal reduction process. And boron of the raw material was saved in residue that could be used as raw materials to produce non-alkali glass fiber. Environment cannot be polluted during this process, as well as the process can create great economic value. Calcined material and residue were taken XRD analysis. Based on thermodynamic analysis, the Gibbs free energy and critical temperature of reduction ascharite with aluminum were calculated. As a result, the critical temperature is 1302℃ at ordinary pressure, and addition, the critical temperature will reduce farther when the air pressure is reduce in the retort, The recovery rate was effected remarkably by the mass of reductant and the making briquettes pressure.

Introduction

Currently the ascharite mineral is used to produce borax by carbon dioxide-soda process in China. The boron utilization rate is lower than 75%. At the same time, magnesium resource and the rest boron is remained in the residue, named boron mud, which has never been utilized [1]. In this paper, magnesium was extracted from ascharite mineral by vacuum thermal reduction process, and other components were kept in the residue, which can be used to manufacture non-alkali glass fiber. It avoids pollution of boron mud and effectively utilizes the resource.

Ma Lihong [2] and Xu Dong [3] have studied the vacuum thermal extraction magnesium from ascharite mineral. However, the material they used contained lower amounts of boron and magnesium. As a result, the magnesium's recovery rate was very low and the content of boron in residue was very low too, so that the residue was low value. Wu X L [4] and Peng J P[5] has made researches on vacuum thermal extract magnesium from rich-boron and rich-Mg mineral with silicon and CaC_2 as reductant, respectively. While silicon serving as reductant needs adding a lot of CaO, the boron in the residue gotten was diluted. The reduction test was also undesired because the reductive ability of CaC_2 was poor.

In this paper, aluminum powder was chosen as reductant because it highly reducing in nature and it needs little CaO in contrast with Si.

Experiments

Experiment materials

The chemical compositions of ascharite mineral, from Kuandian, Liaoning province, are shown in table 1.

Table1 Chemical compositions of ascharite mineral

Chemical composition	MgO	B_2O_3	SiO_2	CaO	Al_2O_3	Others
Content (%.ω)	44.67	26.08	6.18	3.19	1.43	18.45

Other materials including aluminum powder, $CaCO_3$ and CaF_2 are reagents which are produced by Tianjin Kemio Chemical Reagent Co., LTD Production. Particle sizes are less than 74 μm, 100%.

In each test, 80 g ascharite mineral powder was mixed with 151.10 g $CaCO_3$ prior to compaction into several briquettes by 45 MPa. Then these compacted briquettes were fed into a resistance furnace and calcined at 1000℃ for 30 min to eliminate H_2O and CO_2. Then the calcined material is milled to -120 μm particle. Figure 1 shows the XRD pattern of the calcined material.

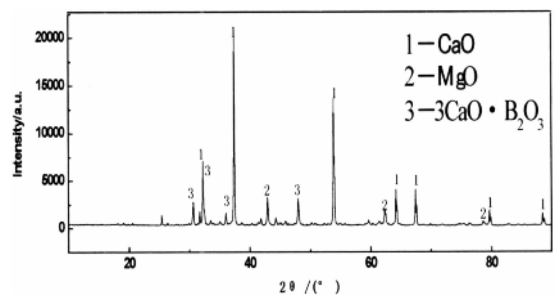
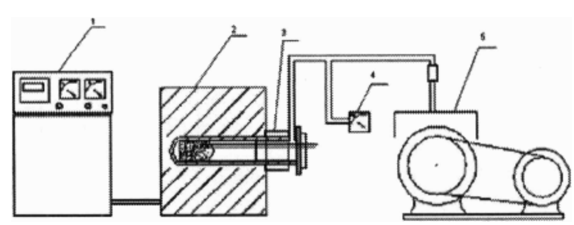


Fig.1 XRD pattern of calcined szaibelyite mineral and $CaCO_3$

According to the Fig 1, the calcined material mainly contains CaO, MgO and $3CaO{\cdot}B_2O_3$.

Equipment

The equipments in experiments mainly included resistance furnace, temperature detection and control system, vacuum system, reduction equipment and cooling system. The sketch of equipments is shown as Fig 2.



1-Tempareture controlling unit, 2-Reduction furnace, 3-Retort, 4-Vacuum gauge, 5-Vacuum pump
Fig.2 Schematic diagram of experimental apparatus

Experiment Process

The test outline is summarized in the figure below and follows the typical Pidgeon process flow sheet.

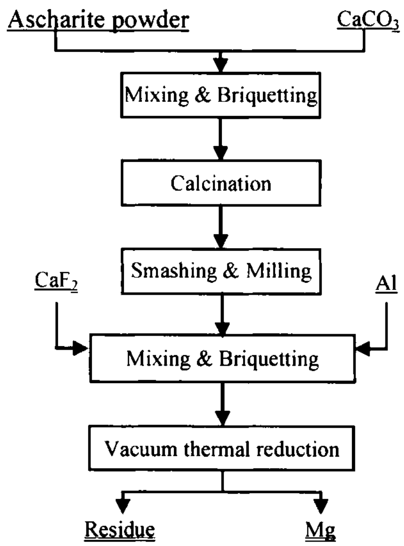


Fig.3 Flow sheet of experiment

The influence of the Al mass and the briquetting pressure prior to reduction on recovery rate was studied in the experiment. In each test, 80 g ascharite mineral powder was mixed with 151.10 g $CaCO_3$. Then the mixed material were compacted into briquettes and undergone calcination. The calcined material was milled and mixed with different mass Al and 5.07 g CaF_2, and then the mixed material for reduction tests was compacted into briquettes as 30MPa pressure. Then the influence of the Al mass on recovery rates was researched. At last confirm the charge mass of Al was 18.28 g in each test.

Second part of the experiment, keeping the conditions as before, only changing the briquetting pressure of reduction material, the influence of briquetting pressure on recovery rate was studied.

All experiments were done at 1200℃ for 120 min, and within vacuum system pressure of 4 Pa.

The method of calculating recovery rate

Before reduction, the magnesium collector was weighed as m_0: After reduction, the collector was weighed again as m_1. So the recovery rate S_1 was calculated as following formula,

$$S_1=(m_1-m_0)/m^*\times 100\% \quad (1)$$

where m^* is the mass of magnesium, which can be calculated based on the mass of ascharite mineral contented in the briquettes.

Results and analysis

The productions and thermodynamic analysis

The experiment produces include magnesium condensed and rich-boron residue. The chemical composition of magnesium condensed is shown in table 2:

Table 2 Chemical analysis result of prepared magnesium compare with ISO Mg-99.8

	Mg	Fe	Si	Ni	Cu	Al	Mn
Experimental value (%)	99.87	0.027	0.005	0.003	0.011	0.039	0.037
ISO (%)	99.80	0.05	0.05	0.002	0.02	0.05	0.1

It can be see that the produced magnesium in experiments is almost accord with the ISO.

Figure 4 shows the XRD pattern of the reduction residue from the reduction experiment with 18.28 g Al and 30MPa briquetting pressure.

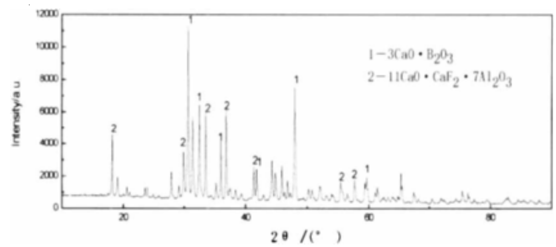


Fig.4 XRD pattern of residue

According to the fig 4, main components of the residue are $3CaO\cdot B_2O_3$ and $11CaO\cdot CaF_2\cdot 7Al_2O_3$. The residue can be used to produce non-alkali glass fiber because it is rich-boron. The chemical compositions of the residue and non-alkali glass fiber are shown in table 3.

Table 3 Chemical composition of experimental residue and non-alkali glass fiber, (%.ω)

	MgO	B_2O_3	SiO_2	CaO	Al_2O_3	Others
Experimental residue	3.49	14.7	3.00	56.42	21.89	0.50
Non-alkali glass fiber	4.5±0.5	8.8±0.5	54.1±0.5	16.6±0.3	14.6±0.4	

According to the table 3, the content of B_2O_3 in residue is higher than non-alkali glass fiber's demand. The other compositions in residue are also needed in glass fiber.

Fig 4 shows that the MgO is deoxidized and that the $11CaO\cdot CaF_2\cdot 7Al_2O_3$ is made in experiment. The reaction equation of deoxidizing MgO is shown as following:

$$12CaO_{(s)} + 21MgO_{(s)} + 14Al_{(l)} = 21Mg_{(g)} + 12CaO\cdot 7Al_2O_{3(s)} \quad (2)$$

ΔG_2^{θ} =3567815-2265.55T (J/mol).

At standard atmospheric pressure, the critical reaction temperature of equation (2) is 1302℃. If the system pressure is 10132.5Pa, the Gibbs free energy of equation (2) will be changed as following:

$$\Delta G_2 = \Delta G_2^{\theta} + 21RT\ln(p_{Mg}/p^{\theta}) = 3567815 - 2667.57\,T \text{ (J/mol)}$$

As a result, the critical reaction temperature falls to 1062℃. In experiments the system pressure usually was 4 Pa or even low, and the temperature in retort was 1200℃ the conditions in experiments can meet the thermodynamic demands.

The relationship between reductant mass and recovery rate

According to the chemical compositions of ascharite mineral in table 1, there are 35.74g MgO in 80g ascharite mineral. Based on the reaction equation (2), the stoichiometric requirement of Al is 16.08g, but in experiments the Al mass usually is above the stoichiometric requirement. Let the Al mass above 16.08g rate is μ, and the μ is counted by the following formula:

$$\mu=(M-16.08)/16.08\times 100\% \qquad (3)$$

where M is the addition mass of Al in test, g. The results are shown in the table 4:

Table 4 The recovery rate obtained by different Al mass experiments

No.	μ(%)	Al (g)	$CaCO_3$ (g)	Recovery rate (%)
1	3.36	16.62	147.98	84.86
2	5.97	17.04	148.76	87.67
3	8.52	17.45	149.54	89.44
4	11.13	17.87	150.33	92.26
5	13.68	18.27	151.11	93.62

According to table 4, with the increasing of Al mass, the chance of Al contact with MgO is increased that performs as the material activity is increased and the recovery rate is improved.

Influence of briquetting pressure on recovery rate

Keeping the experimental conditions as before, with 18.28 g Al, changes the briquetting pressure of reduction material. The briquetting pressures of reduction material and the recovery rates are shown in table5.

Table 5 The recovery rate obtained by different briquetting pressure experiments

No.	Briquetting pressure (MPa)	Recovery rate (%)
1	not being compacted	82.53
2	15	88.86
3	30	93.62
4	45	90.48
5	60	87.51

The test No. 1 means that the calcined material powder didn't be compacted and was directly feed in retort for reduction test. According to the theory of Pidgeon process, which is the method currently to extract magnesium, if the material not be compacted, only a little magnesium is gotten.

However in the test No.1 of table 5, Al and ascharite mineral is melt at the experiment temperature, so it still can obtain a high recovery rate because mass and heat transfer in liquid state is easier than in solid state. According to table 5, the best briquetting pressure is about 30 MPa, and under this condition, the highest recovery rate can reach 93.62%. When the briquetting pressure continues growing up the recovery rate will fall.

Conclusions

There are a lot of B_2O_3 in the residue which can be used to produce non-alkali glass fiber.

Based on thermodynamic analysis, with Al as reductant and enough CaO, the critical temperature is 1302℃. If the pressure in retort is 10132.5Pa, the critical temperature will be 1064℃. So the reaction under experiment conditions can progress well.

It is proved by experimental results shows that the recovery rate can be increased by increasing the mass of Al. With 151.10 g $CaCO_3$, 5.07 g CaF_2 and 80 g ascharite mineral in each test, the reasonable addition mass of Al is 18.27 g.

The results show that it is not necessary to compact the calcined material powder to achieve high magnesium recovery rate. The reasonable briquetting pressure is 30 MPa, and the recovery rate can reach 93.62%.

Acknowledgement

The authors wish to thank the financial support provided by the Fundamental Research Funds for the Central Universities (N100302009).

References

1. Wu X L, Feng N X, Peng J P, et al. Vacuum Thermal Extract Magnesium from Boron Mud [A]. Nyberg E A, Agnew S R, Neelameggham M R, et al. Magnesium Technology Symposium, Magnesium Technology 2009 [C]. San Francisco: TMS, 2009. 61–63.
2. Ma Lihong. Experiment research on thermal reduction magnesium with ascharite minerals [D]. Shenyang: Northeastern University, 2007. 27.
3. Xu Dong, Zhang Xianpeng, Li Jie, et al. Experimental Investigation on Vacuum-Thermal Reduction of Ascharite with Silicon-Aluminum Alloy as Reductant [J]. Journal of Northeastern University (Natural Science), 2008, 29(10): 1455–1458.
4. Wu X L, Feng N X, Peng J P, et al. Experimental Study on Vacuum Thermal Reduction of Ascharite Mineral with Silicon as Reductant [J]. The Chinese Journal of Process Engineering, 2011, 11 (4): 294-298.
5. Peng J P, Wu X L, Zhou S G, et al. Experimental Study on Vacuum Thermal Reduction of Ascharite Mineral with Calcium Carbide as Reductant [A]. Vacuum Technology and Surface Engineering-Proceedings of the 10th Vacuum Metallurgy and Surface Engineering Conference, Vacuum Engineering Conference 2011 and Vacuum Consultancy Workshop 2011 [C]. Beijing: Publishing House of Electronic Industry, 2011. 5