

**J. Cent. South Univ.** (2023) 30: 1179–1190 **DOI:** https://doi.org/10.1007/s11771-023-5311-y

Description Springer

## Leaching kinetics of magnesium from spent magnesia-chromium refractories

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Abstract: In this study, the microscopic properties of spent magnesia-chromium refractories before and after leaching were detected by SEM-EDS and BSE. In addition, the influence of conditions on magnesium leaching was studied by leaching kinetics test, and the kinetics of the leaching process was analyzed by statistical and graphical methods. The results indicate that the relationship between different phases in raw material is complicated that the leaching residue is chromite spinel, and the particles have various holes and cracks. Increasing temperature, hydrochloric acid concentration and liquid-solid ratio can accelerate leaching velocity of magnesium, thereby promoting the whole leaching process, and the promotion effect of temperature is the most significant. The process of leaching magnesium from spent magnesia-chromium refractories conforms to the progressive-conversion model with chemical reaction being the rate-controlling step, in which the corresponding apparent activation energy was 69.11 kJ/mol, and its kinetic equation can be expressed as follows:  $X/(1-X)=4.898 \times 10^8 \times C_{HCI}^{0.7407} \times e^{-8312/T} \times t^{0.9276}$ .

Key words: spent magnesia-chromium refractories; microscopic characteristics; leaching of magnesium; leaching kinetics

**Cite this article as:** LI Wei, JIAO Fen, YANG Cong-ren, XUE Kai, QIN Wen-qing. Leaching kinetics of magnesium from spent magnesia-chromium refractories [J]. Journal of Central South University, 2023, 30(4): 1179–1190. DOI: https://doi.org/10.1007/s11771-023-5311-y.

## **1** Introduction

Magnesia-chromium refractory is made of periclase and chromite sintered at a high temperature above 1500 °C, and its main phases are magnesia and chromite spinel. It has been widely used in non-ferrous metallurgy and other hightemperature process industries because of its excellent properties, and there are currently no other refractory materials that can replace it [1 - 2]. Nevertheless, in the harsh environment of a non-ferrous smelting furnace, the working face of the refractory is directly in contact with various oxide slag, metal melt and sulphide melt, and is affected by various factors such as chemical, thermodynamic

Foundation item: Project(51974364) supported by the National Natural Science Foundation of China; Project(2020YFC1909203) supported by the National Key R&D Program of China; Project (2018TP1002) supported by the Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources, China

Received date: 2022-07-14; Accepted date: 2023-02-27

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and mechanical, resulting in a short service life and high replacement frequency [3-6]. Consequently, a large amount of spent magnesia-chromium refractories is produced. It is estimated that the world's spent refractories can reach 28 million tons annually, and China's spent magnesia-chromium refractories are more than 4 million tons per year. The element occurrence state, phase intercalation state and particle microstructure of spent magnesiachromium refractories are complex, which determines their utilisation process and efficiency to a certain extent. Some scholars studied the microscopic properties of waste refractory bricks on different surfaces, and analyzed the erosion process of impurity metals as well as the damage mechanism of refractory bricks [7-8]. HAN et al [9-10] studied the mineralogical characteristics of the spent magnesia-chromium refractories from the working face to another side, and found that impurity metals, such as Cu, Ag, Pb, and Bi, penetrated the refractories from cracks to holes. Most metal particles are monomer dissociations, and the amount of them will gradually decrease when going deeper into the refractories. These studies are based on large complete pieces of spent magnesia-chromium refractories, and their detailed microscopic characteristics after crushing and grinding treatment have been less studied.

The research on the recycling of spent magnesia-chromium refractories can be traced back to the 1980s. NAZIRIZADEH et al [11] published a patent for processing spent magnesia-chromium bricks into refractory raw materials in 1985, which is the first patent in the field of spent refractory recycling. Since then, with the improvement of environmental protection awareness in various countries worldwide, related research has been also increased [12-15]. Meanwhile, XUE et al [15] used magnesium chloride to volatilize the impurity metals in waste magnesia-chromium refractories, and the volatile slag can be used as an ingredient for regeneration magnesia-chromium refractories. BENNET et al [16-17] found that waste magnesia carbon bricks can be added to the electric arc furnace after selecting and crushing, which is conducive to improving the foaming conditions of the slag and reducing energy consumption. We have developed an efficient and recyclable process to recover all valuable metals in spent magnesiachromium refractories. Firstly, high-value metals such as Cu, Ag, Pb and Bi can be recovered in advance by gravity separation combined with flotation. The recovery rate of Cu and Ag can reach more than 95%, and that of Pb and Bi can reach more than 80% [9 – 10]. Then, the beneficiation tailings are leached with hydrochloric acid combined with ferric chloride, and Cr, Fe and Al are enriched and can be recovered in leaching residue in the form of chromite spinel [18]. Finally, the leaching solution is treated by iron powder reduction to remove impurity metals. So Fe and Mg recovered by goethite hydrolysis are and evaporative crystallisation, respectively [19]. Leaching is the most critical step in this process. Thus, the mechanism of the hydrochloric acid and ferric chloride is revealed to promote the leaching process from the perspective of thermodynamics. However, the kinetics of the leaching process has not been understood. The main component of spent magnesia-chromium refractories is magnesium, and the main reaction of the leaching process is the leaching of magnesium. Thus, studying the leaching kinetics of magnesium can identify the factors affecting the leaching rate of magnesium and the control step of the leaching process, and then appropriate measures can be taken to strengthen the leaching process of magnesium. With the increase in magnesium leaching rate, impurity metals can be exposed and react with the leaching agent earlier and faster, which can strengthen the whole leaching process and improve the overall leaching rate.

This study investigated the microscopic characteristics of spent magnesia-chromium refractories before and after leaching, and the effects of temperature, hydrochloric acid concentration, and liquid-to-solid ratio on the leaching rate of magnesium. The kinetic model of the magnesium leaching process from spent magnesia-chromium refractories was confirmed, then the control step was found, and finally, the leaching kinetic equation was proposed.

## 2 Experimental

## 2.1 Materials

The beneficiation tailings of spent magnesiachromium refractory bricks were the raw materials used in this study, which were obtained from the

silver converter in a smelter in Hunan province, China. The leaching residue was obtained under the following optimal leaching conditions: hydrochloric acid concentration of 4.0 mol/L, liquid-to-solid ratio of 7:1, ferric chloride dosage of 4%, leaching temperature of 70 °C, leaching time of 90 min and stirring intensity of 500 r/min [18]. Table 1 lists the chemical composition of raw material and leaching residue, which were analyzed by X-ray fluorescence spectroscopy (XRF, ZSX Primus II, Rigaku, Japan). The microscopic properties of raw material and leaching residue were analyzed by scanning electron coupled with energy microscopy dispersive spectroscopy and backscattered electron imaging analysis (SEM/EDS/BSE, JSM-IT300LA, JEOL, Japan). Hydrochloric acid (HCl 36.0%-38.0%) was supplied by Wuhan Yongfa Chemical Manufacturing Co., Ltd., Hubei province, China. Ferric chloride (FeCl<sub>3</sub> 99.0%) was purchased from Macklin Biochemical Co., Ltd., Shanghai, China. Deionized water was used in the experiments.

 
 Table 1 Chemical composition of raw material and leaching residue
 wt%

Material	Mg	Cr	Fe	Al	Pb
Raw material	30.29	10.86	6.03	3.2	4.13
Leaching residue	9.95	31.16	14.62	9.56	0.18
Material	Bi	Sb		Cu	Ag
Raw material	2.22	1.52	2	0.63	0.11
Leaching residue	0.01	0.33	;	0.13	0.01

#### 2.2 Experimental procedure

During the test, the water bath was turned on and the temperature required for the test was set; 350 mL of leaching agent was prepared and added to a 500 mL three-necked flask; cooling water was passed into the condenser tube to condense and reflux the volatilised water vapor. When the temperature was stabilized to the set point, the leaching materials were added and the stirrer was turned on to keep the rotation speed at 500 r/min, starting timing; a pipette was used to sample 1 mL of the leachate at regular intervals, and 1 mL of fresh leaching agent was added immediately to maintain. The volume of the solution constant. The leachate sample was filtered and diluted to a certain multiple. The magnesium concentration was analyzed by inductively coupled plasma mass spectrometry (ICP-MS, NexION 2000, PerkinElmer, USA), and the magnesium leaching rate was calculated as:

$$X = \frac{cn}{m\alpha} \times 100\% \tag{1}$$

where c is the concentration of magnesium in the leachate sample; n is the dilution factor; m is the mass of the leaching raw material;  $\alpha$  is the magnesium content in the leaching raw material.

## **3** Results and discussion

#### 3.1 Microscopic characteristics

Microscopic properties such as the element occurrence state, phase intercalation state and particle microstructure of the leaching material have a decisive effect on the leaching process. Analysis and comparison of microscopic properties of the spent magnesia-chromium refractories before and after leaching can provide a mineralogy basis for the analysis of the leaching effect and kinetic process [20–21].

The raw material was detected by SEM-EDS. As shown in Figure 1(a), the shape of the raw material particles was irregular, and the intercalation relationship between different phases was complicated. The dark grey phase (position 1) was magnesia, the light grey phase (position 2) was chromite spinel, and the bright white phase (position 3) included impurity metals such as lead and bismuth, which were primarily conjoined with magnesia and chromite spinel. Figures 1(b) and (c) show enlarged images of some single particles. The raw material particles had various cracks, and there were many small particles of chromite spinel wrapped in magnesia. Thus, the BSE analysis was performed on the particles in Figure 1(a) to further clarify the distribution state of the elements in the raw material, and the results are shown in Figure 2. As shown from the surface scan, the O element in the raw material was evenly distributed in most of the particles. In the surface scans of Mg and Cr, most of Mg and Cr were uniformly present in the magnesia and chromite spinel phases, respectively. The surface scans of Pb, Bi and Sb show that Pb and Bi were in small amounts, closely and evenly coexisting, and Sb was extremely small in amount and unevenly distributed.



Figure 1 SEM mages and EDS analyses of raw materials



Figure 2 BSE analyses of raw materials

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Moreover, the leaching residue was detected by SEM-EDS with the results given in Figure 3. The magnesia and impurity metal phases had disappeared as compared with the raw material, and only the chromite spinel phase remained, which indicated that the leaching effect of magnesium and impurity metals was pretty good. Based on Figures 3(c) and (d), the particles of leaching residue had more pores and cracks than before leaching. Furthermore, the BSE analysis was performed on the particles in the area of Figure 3(a), and the surface scan results in Figure 4 show that the elements O, Cr, Mg, Al, and Fe were uniformly and tightly distributed in the chromite spinel. Particularly, the magnesium in it was formed by replacing part of the iron in the form of isomorphism during the geological mineralisation; hence, this part of the magnesium cannot be leached out.

# **3.2 Effect of leaching conditions on magnesium leaching**

A previous study [18] showed that increasing the dosage of ferric chloride and stirring intensity can significantly promote leaching of Sb, Cu and Ag, but have little effect on leaching of Mg. Therefore, the dosage of ferric chloride and the stirring intensity were fixed at the optimum conditions, and only effects of temperature, hydrochloric acid concentration and liquid-solid ratio on magnesium leaching were investigated. 3.2.1 Effect of temperature

There is an exothermic reaction between magnesium and hydrochloric oxide acid. From the perspective of thermodynamics, the increase in temperature is not conducive to the progress of the reaction; however, from the perspective of kinetics, it is often necessary to carry out leaching at high temperatures to ensure a sufficient leaching velocity [22-23]. The effect of temperature on magnesium leaching was investigated at the hydrochloric acid concentration of 4.0 mol/L and the liquid-to-solid ratio of 7:1. Figure 5 shows the curve of magnesium leaching rate versus time under different temperature conditions, and the slope is the leaching velocity of magnesium. The leaching velocity of magnesium became increasingly faster with an increase in temperature, and gradually slowed down over time. Therefore, increasing the leaching temperature can accelerate the leaching process. 3.2.2 Effect of hydrochloric acid concentration

The acid concentration plays a crucial role in leaching effect in the acid leaching process. However, if it is too low, the leaching speed will be



Figure 3 SEM images and EDS analyses of leaching residue





Figure 5 Effect of temperature on magnesium leaching rate

slow; if it is too high, the leaching will lose its selectivity [24-25]. Therefore, ensuring a suitable acid concentration for leaching is very important. The effect of hydrochloric acid concentration on

magnesium leaching was studied at 70 °C and liquid-to-solid ratio of 7:1. The curve of magnesium leaching rate versus time under different hydrochloric acid concentration is shown in Figure 6. As seen, the leaching velocity became increasingly faster with the increase in hydrochloric acid concentration, and gradually slowed down over time. The influence of hydrochloric acid concentration on the leaching process was slightly less as compared with temperature.

3.2.3 Effect of liquid-to-solid ratio

The liquid-to-solid ratio is an important parameter in the leaching process. Increasing the liquid-to-solid ratio is conducive to reducing the viscosity of the leaching system, increasing the efficiency of diffusion and mass transfer, which is beneficial to the improvement of the leaching rate [26-27]. The effect of the liquid-to-solid ratio on magnesium leaching was examined under the



Figure 6 Effect of hydrochloric acid concentration on magnesium leaching

conditions of a hydrochloric acid concentration of 4.0 mol/L, and leaching temperature of 70 °C. As shown in Figure 7, the trend of magnesium leaching rate changing with time under different liquid-to-solid ratios was similar to that under different hydrochloric acid concentrations, that is, with the increase of the liquid-to-solid ratio, the leaching velocity gradually increased; however, the extent of increase was smaller than that of temperature.



Figure 7 Effect of liquid-to-solid ratio on magnesium leaching

## 3.3 Kinetics of magnesium leaching

#### 3.3.1 Kinetic model

The leaching kinetic model is established based on ideal conditions, and it reveals the reaction process from a macroscopic level. The unreacted shrinking core model is the most common model in liquid-to-solid reactions; thus it is suitable for the leaching of low-grade, dense and void-free ores, and the size of solid particles remains unchanged after the reaction [28 - 30]. The progressive-conversion model is based on the fact that most solid reactant particles are loose and porous, and diffusion and reaction of the liquid reactant always occur simultaneously within the solid particles until the entire reactable portion of the solid particles is fully reacted [31]. Based on the analysis of the microscopic properties of the spent magnesiachromium refractories, the magnesia and chromite spinel were inlaid and wrapped in complex before leaching, and the particles had various cracks. After leaching, the magnesia was completely leached, and the leaching residue was chromite spinel with more holes and cracks. Therefore, the kinetic process of magnesium leaching from spent magnesiachromium refractories does not conform to the unreacted shrinking core model, but conforms more to the progressive-conversion model, in which the leaching kinetic equations can be represented by pseudo-first-order and pseudo-second-order models [19, 32], as follows:

Pseudo-first-order: 
$$-\ln(1-X) = k_1 t^n$$
 (2)

Pseudo-second-order: 
$$\frac{X}{1-X} = k_2 t^n$$
 (3)

where *X* is the leaching rate of the reactant;  $k_1$  and  $k_2$  are the apparent reaction rate constants (min<sup>-*n*</sup>); *t* is the reaction time (min); *n* is a constant related to the properties of the reactant particles.

The data points in Figures 5–7 were substituted into the two equations of the progressiveconversion model for fitting analysis. As can be seen from the fitting curves and results under different leaching conditions shown in Figure 8 and Table 2,  $\ln[X/(1-X)]$  versus lnt had a better linear fitting relationship under different temperature, hydrochloric acid concentration and liquid-to-solid ratio conditions, and the correlation coefficients of  $\ln[X/(1-X)]$  versus lnt were higher than 0.99 under all conditions. Therefore, the leaching process of magnesium conformed to the pseudo-second-order model of the progressive-conversion model.

#### 3.3.2 Kinetic equation

In order to quantitatively express the relationship between leaching temperature, hydrochloric acid concentration and liquid-to-solid ratio on magnesium leaching rate [33 – 34], the





**Figure 8** Fitting curves of  $\ln[X/(1-X)]$  versus  $\ln t$  under different temperatures (a), hydrochloric acid concentrations (b) and liquid-solid ratios (c)

Table 2 Fitting results under different leaching conditions

Leaching parameter		Regression equation	Correlation coefficient, R <sup>2</sup>
Temperature/°C	40	ln[X/(1-X)]=0.9975lnt-4.0625	0.9990
	50	$\ln[X/(1-X)] = 1.0260 \ln t - 3.2320$	0.9986
	60	$\ln[X/(1-X)]=0.98411nt-2.3654$	0.9964
	70	$\ln[X/(1-X)]=0.9896\ln t - 1.7740$	0.9974
Hydrochloric acid concentration/(mol·L <sup>-1</sup> )	2.5	$\ln[X/(1-X)] = 0.7526 \ln t - 2.1826$	0.9921
	3.0	$\ln[X/(1-X)]=0.8358\ln t - 1.9850$	0.9915
	3.5	$\ln[X/(1-X)]=0.9156\ln t - 1.9091$	0.9930
	4.0	$\ln[X/(1-X)]=0.9989\ln t - 1.7947$	0.9949
Liquid-to-solid ratio	4:1	$\ln[X/(1-X)] = 0.7287 \ln t - 2.3700$	0.9953
	5:1	$\ln[X/(1-X)]=0.8819\ln t - 2.1729$	0.9984
	6:1	$\ln[X/(1-X)]=0.9847\ln t - 2.0864$	0.9982
	7:1	$\ln[X/(1-X)] = 1.0352 \ln t - 1.9396$	0.9984

leaching kinetic equation was proposed based on the progressive-conversion pseudo-second-order model as follows:

$$\frac{X}{1-X} = k C^a_{\rm HCI} \left(\frac{\rm L}{\rm S}\right)^b {\rm e}^{\frac{-E_s}{RT}} t^n$$
(4)

where k is the reaction rate constant; X is the magnesium leaching rate;  $C_{\text{HCI}}$  is the hydrochloric acid concentration; L/S is the liquid-to-solid ratio; T is the leaching temperature; t is the reaction time;  $E_{\text{a}}$  is the apparent reaction activation energy; R is the molar gas constant; a, b and n are the exponents of

the corresponding parameters.

When the hydrochloric acid concentration and liquid-to-solid ratio were constant and only the temperature changed, the leaching rate was a function of temperature and time; hence, the above formula can be rewritten as follows:

$$\frac{X}{1-X} = k_3 \mathrm{e}^{\frac{-E_s}{RT}} t^n \tag{5}$$

where  $k_3$  is the reaction rate constant. Taking the logarithm of Eq. (5) can get:

$$\ln\left(\frac{X}{1-X}\right) = \ln k_3 - \frac{E_a}{RT} + n\ln t \tag{6}$$

 $\ln k_3 - E_a/(RT)$  was equal to the constant term of equation the regression under temperature conditions in Table 2. The plot of  $\ln k_3 - E_a/(RT)$ versus 1/T is drawn in Figure 9. The slope of the fitted line was  $-E_a/R$ , hence, the apparent reaction activation energy  $E_a=69.11$  kJ/mol was calculated, this value of magnesium leaching process was high and the similar results were given by OZDEMIR et al [32] and RASCHMAN et al [35]. The leaching rate rapidly increased with an increase in temperature, and the stirring intensity had no evident effect on the leaching rate. Therefore, the control step of the leaching process of magnesium from spent magnesia-chromium refractories was the chemical reaction.



**Figure 9** Plot of  $\ln k_3 - E_a/(RT)$  versus 1/T

When the temperature and liquid-to-solid ratio were constant and only the hydrochloric acid concentration changed, the leaching rate was a function of hydrochloric acid concentration and time, hence, Eq. (4) can be rewritten as:

$$\frac{X}{1-X} = k_4 C_{\rm HCl}^a t^n \tag{7}$$

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where  $k_4$  is the reaction rate constant. Taking the logarithm of Eq. (7) can get:

$$\ln\left(\frac{X}{1-X}\right) = \ln k_4 + a \ln C_{\rm HCl} + n \ln t \tag{8}$$

 $\ln k_4 + a \ln C_{\rm HCl}$  was equal to the constant term of the regression equation under hydrochloric acid concentration conditions in Table 2. From the plot of  $\ln k_4 + a \ln C_{\rm HCl}$  versus  $\ln C_{\rm HCl}$  given in Figure 10, the slope of the fitted line was *a*; thus, we got *a*=0.7982.



Figure 10 Plot of  $\ln k_4 + a \ln C_{HCl}$  versus  $\ln C_{HCl}$ 

Similarly, when the temperature and hydrochloric acid concentration were constant and only the liquid-to-solid ratio changed, the leaching rate was a function of the liquid-to-solid ratio and time; thus, Eq. (4) can be rewritten as follows:

$$\frac{X}{1-X} = k_5 \left(\frac{\mathbf{L}}{\mathbf{S}}\right)^b t^n \tag{9}$$

where  $k_5$  is the reaction rate constant. Taking the logarithm of Eq. (9) can get:

$$\ln\left(\frac{X}{1-X}\right) = \ln k_{\rm s} + b \ln\left(\frac{\rm L}{\rm S}\right) + n \ln t \tag{10}$$

 $\ln k_s + b \ln(L/S)$  was equal to the constant term of the regression equation under liquid-to-solid ratio conditions in Table 2. From the plot of  $\ln k_s +$  $b \ln(L/S)$  versus  $\ln(L/S)$  given in Figure 11, the slope of the fitted line was *b*; thus, we got *b*=0.7407.

In Figures 5–7, n is the slope of each fitted line in Figure 8. Based on the corresponding values in Table 2, the average value of n can be obtained as 0.9276. The values of  $E_a$ , a, b, and n were



**Figure 11** Plot of  $\ln k_5 + b \ln(L/S)$  versus  $\ln(L/S)$ 

substituted into Eq. (4), and then this formula was used to fit the data points in Figures 5–7. From the plot given in Figure 12, the slope of the fitted line was k, and the value of k can be obtained as  $4.898 \times 10^8$ . Finally, the kinetic equation of magnesium leaching can be determined as:

$$\frac{X}{1-X} = 4.898 \times 10^8 \times C_{\rm HCl}^{0.7982} \times \left(\frac{\rm L}{\rm S}\right)^{0.7407} \times e^{\frac{-8312}{T}} \times t^{0.9276}$$
(11)



Figure 12 Plot of X/(1 - X) versus  $C_{\text{HCl}}^{0.7982} \times (\text{L/S})^{0.7407} \times e^{-8312/T} \times t^{0.9276}$ 

## 4 Conclusions

1) Leaching raw material of spent magnesiachromium refractories is irregular in shape and has various cracks. The relationship between different phases is complicated, and various small particles of chromite spinel are wrapped in magnesia. The leaching residue particles have more holes and cracks, all of which are chromite spinel, and the magnesium in it existed in the form of isomorphism; hence, it cannot be leached.

2) The influence trends of temperature, hydrochloric acid concentration and liquid-to-solid ratio on magnesium leaching are similar. With these parameters increasing, the magnesium leaching speed gradually becomes faster and then gradually becomes slower over time. Increasing temperature, hydrochloric acid concentration and liquid-to-solid ratio can accelerate the leaching process, and the promotion effect of temperature is the most significant.

3) The process of leaching magnesium from spent magnesia-chromium refractories conforms to the pseudo-second-order model of the progressive-conversion model, and the control step is the chemical reaction. Its apparent reaction activation energy is 69.11 kJ/mol, and its kinetic equation can be expressed as follows:  $X/(1-X)=4.898\times10^8\times C_{\rm HCl}^{0.7982}\times(L/S)^{0.7407}\times e^{-8312/T}\times t^{0.9276}$ .

## Contributors

LI Wei provided literature research, formal analysis and writing-original draft. JIAO Fen provided funding acquisition, project administration and data curation. YANG Cong-ren provided methodology, writing-reviewing and editing. XUE Kai provided validation, resources and formal analysis. QIN Wen-qing provided supervision and funding acquisition.

#### **Conflict of interest**

LI Wei, JIAO Fen, YANG Cong-ren, XUE Kai, QIN Wen-qing declare that they have no conflict of interest.

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(Edited by FANG Jing-hua)

## 中文导读

## 废弃镁-铬耐火材料中镁的浸出动力学

**摘要:**本研究采用 SEM-EDS 和 BSE 对废弃镁-铬耐火材料浸出前后的微观特性进行了检测,通过浸出 动力学试验研究了浸出条件对镁浸出的影响,采用统计和作图法对镁的浸出过程进行了动力学分析。 结果表明,原料中不同物相之间嵌布关系复杂,浸出渣为铬铁尖晶石且颗粒中存在各种孔洞和裂纹。 升高温度、增加盐酸浓度和液固比可以加快镁的浸出速度,从而促进整个浸出过程,其中温度的促进 作用最强。最终确定废弃镁-铬耐火材料中镁的浸出过程符合渐进转化模型,其控制步骤为化学反应, 表观活化能为69.11 kJ/mol,动力学方程为: *X*/(1-*X*)=4.898×10<sup>8</sup>×C<sup>0.7982</sup>×(L/S)<sup>0.7407</sup>×e<sup>-8312/7</sup>×t<sup>0.9276</sup>。

关键词: 废弃镁-铬耐火材料; 微观特性; 镁浸出; 浸出动力学

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