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Dissolution Kinetics of Magnesium from Calcined Serpentine in NH_4Cl Solution

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ABSTRACT: A process of extracting magnesium from serpentine to produce Mg compounds by using recyclable NH_3 was proposed. This process includes calcination of serpentine; dissolution of magnesium by NH_4Cl leaching to obtain NH_3 and MgCl_2 -rich solution, and precipitation of $\text{Mg}(\text{OH})_2$ from refined MgCl_2 -rich solution by feeding NH_3 . The effects of various factors, such as roasting temperature and time, particle size, concentration of NH_4Cl solution, solid-to-liquid ratio, and leaching temperature, on the dissolution kinetics of magnesium of the calcined serpentine were comprehensively investigated. It is found that the extraction rate of magnesium was enhanced by the removal of NH_3 generated from the reaction system. Thus, the obtained optimum conditions for magnesium extraction from serpentine are a roasting temperature of 700 °C, a roasting time of 1 h, a particle size fraction of $-0.20 + 0.10$ mm, an initial ammonium chloride concentration of 4.0 M, a solid-to-liquid ratio of 20/500 g/mL, and a reaction temperature of 104 °C. With the removal of NH_3 in batch leaching study, the maximum recovery of magnesium reached 83.87%, and the concentration of magnesium was $\sim 0.63 \text{ mol}\cdot\text{L}^{-1}$, satisfying the requirement of $\text{Mg}(\text{OH})_2$ precipitation. Finally, the reaction kinetics of the system was successfully modeled by an empirical diffusion-like equation. The apparent activity energy was obtained to be $23.56 \pm 1.06 \text{ kJ}\cdot\text{mol}^{-1}$. The results from this study provide the fundamentals for magnesium extraction from serpentine by NH_4Cl leaching.

1. INTRODUCTION

Serpentine, $[\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4]$, a hydrated magnesium silicate, is abundant around the world. For example, China has considerable serpentine resources, with more than 12 billion tons of proven reserves.¹ Serpentine is characterized by high levels of magnesium (ca. 35 wt % MgO), low calcium and aluminum content (ca. 1–4 wt % CaO and Al_2O_3), and extremely low amounts of sodium and potassium (ca. 0.05 wt % K_2O and Na_2O).² Additionally, an important quantity of nickel and chromium (ca. 0.3 wt % NiO and Cr_2O_3) is also present in serpentine rock.^{3,4} This mineral has been utilized in various applications, such as fertilizer production,⁵ soil amelioration,⁶ extraction of amorphous silicate,⁷ carbon sequestration,⁸ extraction of pure magnesium compounds,^{9,10} and silica production.¹¹

Magnesium and its alloys are attractive materials for the transportation industry because of their low density and high strength. A promising way of magnesium production is the electrolysis of molten anhydrous magnesium chloride.^{12,13} Other application fields¹⁴ such as refractories,^{15,16} also require significant quantities of magnesium related compounds. In the production of pure magnesium compounds and silica from serpentine, an acid extraction technique is usually applied. The acid leaching stage plays a key role in the overall process where magnesium is recovered from the ore. After leaching, the pregnant liquor is purified and refined to obtain magnesium salt for the next application. The most common lixiviants are sulfuric acid, hydrochloric acid, and other inorganic and organic acids. As early as 1942, MacIntire¹⁷ utilized concentrated sulfuric acid in the extraction of magnesium from serpentine. Kosuge et al.¹⁸ reported that the magnesium extractions from

serpentine reached >90% at reaction temperature ~ 100 °C, sulfuric acid concentration 4 M, and 8 h reaction time. Alexander et al.¹⁹ considered the relative contributions from sulfuric acid concentration, particle size, and reaction time for further investigations to extract magnesium from serpentine. Using hydrochloric acid as the leaching agent, Lackner et al.²⁰ studied the indirect carbonation of magnesium from serpentine. Ficara et al.²¹ reported on a novel process for the primary production of magnesium from serpentine tailings by HCl leaching, which was developed at the Noranda Technology Centre in 1986. Then, Dutrizac et al.²² and Teir et al.²³ investigated the effects of hydrochloric acid concentration, leaching temperature, and serpentine particle size on the dissolution of magnesium, respectively. Park et al.²⁴ used various solvents such as orthophosphoric acid, oxalic acid, and ethylenediaminetetraacetic acid (EDTA) to polarize and weaken the magnesium bonds within the serpentine structure and to increase the dissolution of magnesium in hydrochloric acid. Several other acids, including acetic acid and phosphoric acid were investigated by Maroto-Valer et al.²⁵ in an attempt to produce a magnesium-rich solution.

The double-layered structure of serpentine results in an acid–base character, which causes them to be resistant in acidic and alkaline environments. To accelerate the leaching rate, pretreatment methods such as mechanochemical treatment^{26–29} or calcination can be applied to destroy the structure

Received: December 23, 2013

Revised: April 17, 2014

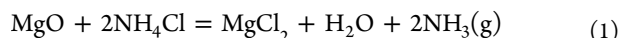
Accepted: April 19, 2014

Published: April 21, 2014



of serpentine. Zhang et al.³⁰ conducted research on acid leaching of serpentine ground for various times at room temperature using 1 M HCl and 1 M H₂SO₄ solutions, respectively, and more than 90% of Mg in the sample ground for 240 min was leached. Fedorocková et al.³¹ explored how calcination temperature and time affect the amount of magnesium dissolved during the initial period of leaching of calcined serpentine in hydrochloric acid.

Strong acid leaching enhances the dissolution of magnesium as well as other undesired elements, such as iron, aluminum, calcium, silicon, and nickel, which makes difficult the subsequent solution purification. As alternative, it may be possible to use weak acid to selectively leach the magnesium from treated serpentine. Pundsack et al.³² reported that the leaching of serpentine in 1.4 M NH₄HSO₄ at 95 °C for about 5 h can give a magnesium extraction of 92.8%. Wang and Maroto-Valer³³ examined the dissolution of serpentine sample in the solutions of ammonium salts, including (NH₄)₂SO₄, NH₄Cl, and NH₄HSO₄. They observed that NH₄HSO₄ was the most efficient among these lixiviants, giving 100% Mg dissolution after 3 h leaching in 1.4 M NH₄HSO₄ at 100 °C. Therefore, NH₄Cl may serve as a lixiviant to extract magnesium from serpentine with the reason that the generated MgCl₂-rich solution is relatively pure and easily to refine. The leaching reaction can be assumed to be



By the experiment, we found that the generated NH₃(g) was the main barrier for the mineral dissolution, and the reaction can run smoothly by the removal of NH₃. The generated NH₃ can be used to precipitate Mg(OH)₂ from the MgCl₂-rich pregnant. Thus, a process of extracting magnesium from calcined serpentine to produce Mg-compounds by using recyclable NH₃ was proposed. Furthermore, more valuable products can be produced from the large reservation of serpentine ore by this process. Lower operating cost may be expected because of the reduced dissolution of undesired elements and the reuse of the lixiviant.

In this work, the dissolution kinetics of magnesium of the calcined serpentine in NH₄Cl solutions is experimentally studied. The influence of various factors, such as roasting temperature and time, particle size of serpentine, concentration of NH₄Cl solution, solid-to-liquid ratio, and leaching temperature, were systematically investigated. Then, a process to extract magnesium from calcined serpentine by NH₄Cl leaching was proposed and verified feasible. Finally, the reaction kinetics of the system were successfully modeled by an empirical diffusion-like equation and the apparent activity energy was calculated.

2. MATERIALS AND METHODS

2.1. Experimental Materials. Bulk serpentine from the Qinghai Honfoo Mining Co. LTD was used in leaching tests. The material was crushed, ground, and sieved using ASTM standard sieves, giving particle size of $-0.20 + 0.10$, $-0.30 + 0.20$, and $-0.40 + 0.30$ mm. Then every sample was calcined to calculate the weight loss. Analytically pure NH₄Cl (>99.5%) was supplied by Xilong Chemical Group. All solutions used in this study were prepared by dissolving analytical-grade chemicals directly without further purification. Stock solutions were prepared in CO₂-free distilled water (conductivity <0.1 μS·cm⁻¹).

2.2. Characterization. The chemical composition was determined by X-ray fluorescence spectrometer (XRF, PANalytical spectrometer). The structure and morphology of the particles were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM; JEOL model JSM-6700F). Powder XRD (X'Pert PRO MPD, PANalytical, Almelo, The Netherlands) patterns were recorded on a diffractometer (using Cu Kα radiation) operating at 40 kV/30 mA. A scanning rate of 0.02°/s was applied to record the patterns in the 2θ angle range of 5–90°. Differential scanning calorimetry and thermal gravimetric analysis (DSC-TGA; PerkinElmer thermogravimetric analyzer) were employed to determine the inherent water content of the sample.

2.3. Experimental Procedure. The serpentine was roasted in a muffle furnace at temperatures ranging from 300 to 900 °C for different time intervals. Then, magnesium extraction experiments were carried out in a 1 L jacketed glass reactor equipped with a water-cooled condenser or a high-pressure batch autoclave according to the reaction temperature, respectively. Both of the reactors were equipped with propeller agitator. The stirring speed was kept at about 300 rpm in all experiments satisfying hydrodynamic requirements of maintaining a stable and intensive enough mixing.

The glass reactor was used for reaction temperature below 104 °C. A typical experimental procedure was performed as follows: NH₄Cl solution (~500 mL) of known concentration was put into the reactor, and the system was maintained at a desired temperature with ±0.1 °C by circulating heating oil through the vessel's jackets. When the desired temperature was reached, a known mass of calcined serpentine sample was added into the reactor. The autoclave was employed when the reaction temperature was over 150 °C. The NH₄Cl solution (~500 mL) with known concentration and the calcined serpentine with certain weight were introduced into the reactor one after another. Then the autoclave was sealed properly, and the system was heated to the desired reaction temperature by electric heating apparatus. All the chemical reagents and samples were weighed with an uncertainty of ±0.01 g.

Liquid samples (~5 mL) were collected at predetermined time intervals, and filtered using 0.22 μm syringe filters. The clear filtrate was analyzed for the concentrations of Mg²⁺ by titration with standard EDTA solution. The conversion ratio of Mg (X) was calculated through the following expression:

$$X = \frac{24Vc_{\text{Mg}}}{mx_{\text{Mg}}} \quad (2)$$

where c_{Mg} is the concentration of Mg²⁺ in the leaching aqueous solution, V is volume of the leaching aqueous solution, and 24 denotes the mole weight of Mg. m is the mass of the added serpentine solids, and x_{Mg} is the fractional content of Mg in the solids.

3. MODELING OF LEACHING KINETICS

Generally, hydrometallurgical leaching operations are controlled by diffusion through the fluid and/or inert solid layer of the reactant or by chemical surface reaction. The slowest of these steps is considered the rate controlling step.

In order to establish the reaction kinetics and rate controlling step for the dissolution of magnesium in NH₄Cl solution, the experimental data were analyzed using the unreacted shrinking core model. The fluid–solid heterogeneous reaction can be represented by reaction 1. According to the shrinking core

model, the reaction is considered to take place first at the outer surface of the particle.³⁴ The region of the reaction goes into the solid and the reacting particle shrinks during the reaction. The rate can be described by film diffusion, chemical reaction, or product layer diffusion characteristics equations, which can be written as follows:

$$\begin{aligned} \text{film diffusion: } x &= 3bM_{\text{Serpentine}}k_1C_{\text{NH}_4\text{Cl}}t/(\rho x_{\text{Serpentine}}R_s x^*) \\ &= k_1t \end{aligned} \quad (3)$$

$$\begin{aligned} \text{product layer diffusion: } 1 - 3(1 - x)^{2/3} + 2(1 - x) \\ = 6bM_{\text{Serpentine}}D_{\text{eff}}C_{\text{NH}_4\text{Cl}}t/(\rho x_{\text{Serpentine}}R_s^2 x^*) = k_2t \end{aligned} \quad (4)$$

$$\begin{aligned} \text{chemical reaction controls: } 1 - (1 - x)^{1/3} &= bM_{\text{Serpentine}} \\ k_3f(C_{\text{NH}_4\text{Cl}})t/(\rho x_{\text{Serpentine}}R_s x^*) &= k_3t \end{aligned} \quad (5)$$

where $M_{\text{serpentine}}$ represents the molecular weight of serpentine, k is the kinetic constant, t indicates the reaction time, ρ means the density of serpentine, R_s , x^* , and D_{eff} represent the radius of particle, maximum conversion ratio of magnesium, and diffusion coefficient in product layer, respectively.

4. RESULTS AND DISCUSSION

4.1. Characterization of Serpentine. The X-ray fluorescence analysis of the serpentine is listed in Table 1. Table 1

Table 1. XRF Analysis of the Serpentine Sample

component	amount, %
MgO	39.04
SiO ₂	45.24
Al ₂ O ₃	3.33
Na ₂ O	0.058
P ₂ O ₅	0.022
SO ₃	0.025
K ₂ O	0.03
CaO	2.83
MnO	0.11
Fe ₂ O ₃	7.40
NiO	0.33
TiO ₂	0.18
Cr ₂ O ₃	0.37
LOI ^a	13

^aLoss on ignition (LOI) is the sample weight loss after being ignited.

shows that the samples contained 39.04% MgO, 45.24% SiO₂, 7.40% Fe₂O₃, and minor elements, such as calcium, aluminum, nickel, manganese, chromium, etc. The DSC-TGA analysis of the serpentine is shown in Figure 1. As it can be seen, there is a slight weight loss by increasing the temperature up to 500 °C, probably due to the evaporation of adsorbed water caused by the heat effect. And at the temperature between 500 and 700 °C, the interlayer water was released and a remarkable weight loss occurred. After that, an endothermic peak was observed at 803 °C, which represents the destruction of serpentine crystalline structure and the formation of new mineral species. Figure 2 displays the XRD patterns of the as-prepared serpentine samples. By increasing the calcination temperature from 25 to 600 °C, the intensity of characteristic peaks (10–25°) from the main phases is getting weaker. At temperatures

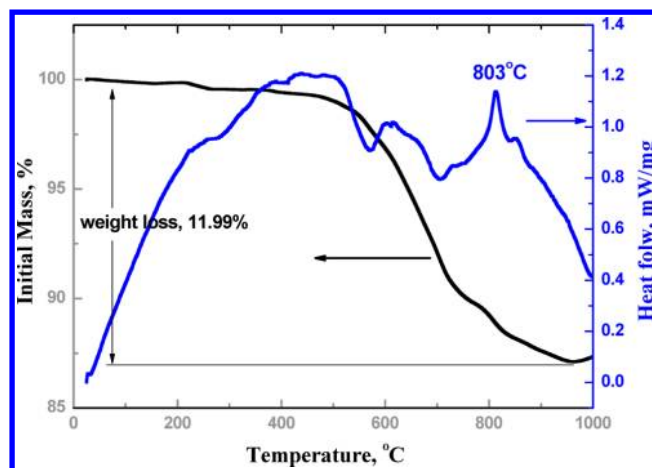


Figure 1. DSC-TGA analysis of the serpentine sample.

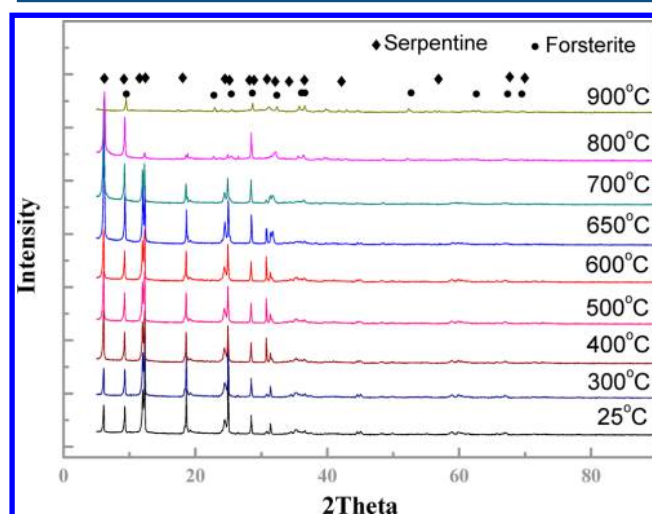


Figure 2. XRD patterns of the serpentine samples calcined at temperatures from 25 to 900 °C.

between 600 and 800 °C, some peaks gradually disappeared and the structure of the calcined serpentine appears to be highly destroyed. When the temperature is above 800 °C, a new phase of forsterite is formed, which is in accordance with the DSC-TGA analysis (Figure 1).

4.2. Effect of Roasting Temperature. Serpentine with the particle size of $-0.20 + 0.10$ mm was roasted at temperatures ranging from 600 to 900 °C for 1 h in a muffle furnace to investigate the effect of roasting temperature on the magnesium extraction. The leaching tests were performed under the conditions of the initial ammonium chloride concentration of 4.0 M, reaction temperature of 70 °C, and solid-to-liquid ratio of 20/500 g/mL. The experimental results are presented in Figure 3. As it can be seen, the initial dissolution rate of magnesium increases rapidly with the reaction time at constant roasting temperature, and the conversion ratios of magnesium reach 4.73% for 600 °C, 7.67% for 650 °C, 11.63% for 700 °C, 10.28% for 800 °C, and 4.00% for 900 °C at 20 min leaching time. With prolonged leaching time, the curves for conversion ratio of magnesium begin to level off. The extraction of magnesium by increasing the calcination temperature from 600 to 700 °C, and decreased gradually with an increase of the calcination temperature to 900 °C. Therefore, the calcination

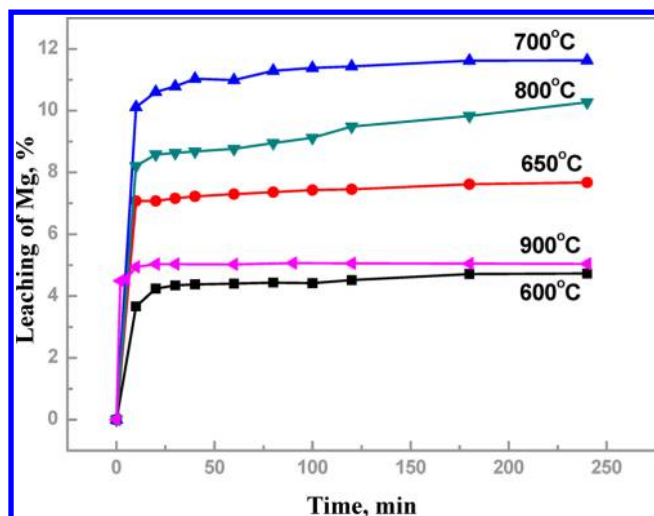


Figure 3. Effect of roasting temperature on magnesium dissolution from calcined serpentine.

temperature of 700 °C was selected as optimum roasting temperature in the following experimental runs.

4.3. Effect of Roasting Time. The influence of roasting time on magnesium extraction was studied under the following conditions: roasting temperature of 700 °C, particle size fraction of $-0.20 + 0.10$ mm, initial ammonium chloride concentration of 4.0 M, reaction temperature of 70 °C, and solid-to-liquid ratio of 20/500 g/mL. The results are given in Figure 4, and it can be observed that roasting time with 2 h yields a maximum value of Mg extraction ($\sim 13.72\%$), which was beneficial to the magnesium extraction from serpentine.

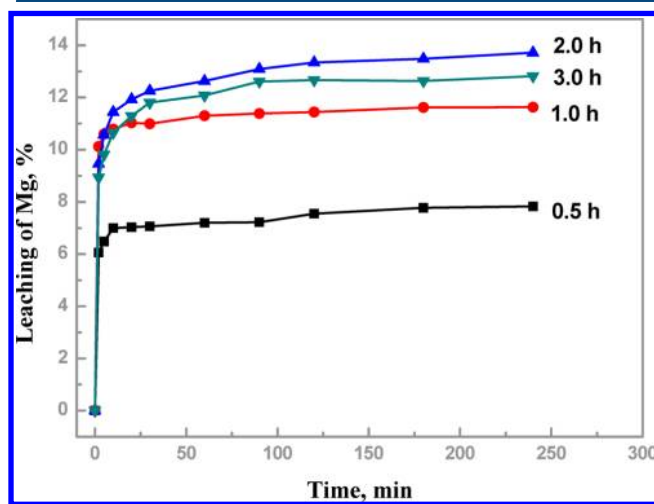


Figure 4. Effect of roasting time on magnesium dissolution from calcined serpentine.

4.4. Effect of Particle Size. The effect of the particle size on the dissolution rate of magnesium was studied using the following size fractions: $-0.20 + 0.10$, $-0.30 + 0.20$, and $-0.40 + 0.30$ mm. The roasting temperature and time, concentration of ammonium chloride, solid-to-liquid ratio, and reaction temperature were kept constant at 700 °C, 2 h, 4.0 M, 20/500 g/mL, and 70 °C, respectively. Figure 5 demonstrated the conversion of Mg as a function of reaction time at different particle size. It is found that the smaller particle size produced a higher Mg conversion ratio. This case can be ascribed to the

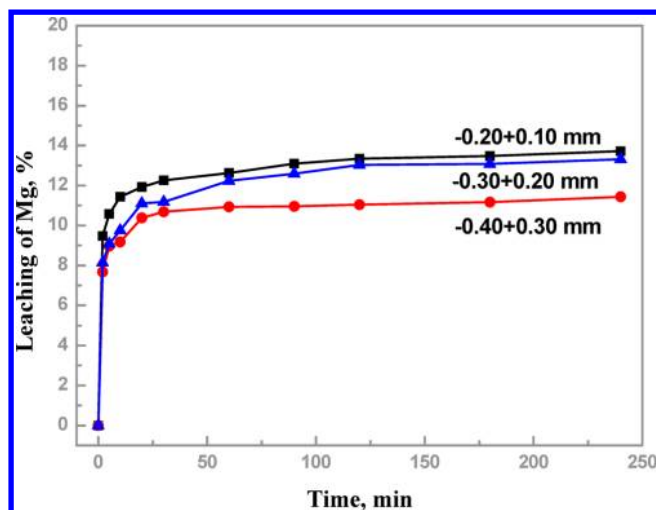


Figure 5. Effect of particle size on magnesium dissolution from calcined serpentine.

increase in the number of particles per unit of solid weight. That is, the increase in the surface area causes more exposure of calcined serpentine to the NH_4Cl solution with the smaller particle.

4.5. Effect of NH_4Cl Concentration. The relationship between the ammonium chloride concentration and the conversion ratio of magnesium was investigated by varying the concentration in the range of 4.0 to 6.0 M. And the leaching experiments were carried out under the conditions of reaction temperature 70 °C, particle size $-0.20 + 0.10$ mm and solid-to-liquid ratio 20/500 g/mL. The leaching results were plotted in Figure 6, and decreased magnesium conversion has been

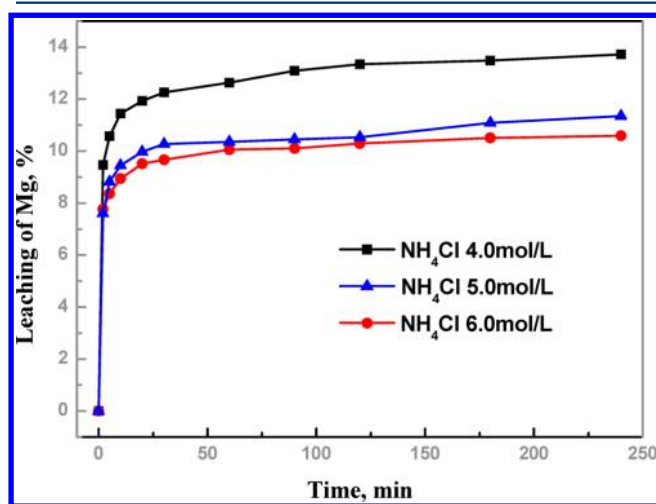


Figure 6. Effect of ammonium chloride concentration on magnesium dissolution from calcined.

observed with an increasing of initial NH_4Cl solution concentration. For example, the extractions of magnesium reached 13.72% for 4.0 M, 11.35% for 5.0 M, and 10.59% for 6.0 M NH_4Cl concentration after leaching for 240 min.

4.6. Effect of Solid-to-Liquid Ratio. The solid-to-liquid ratio varied from 5/500 to 20/500 g/mL was adopted to investigate the effect of solid-to-liquid ratio. In these experiments, NH_4Cl solution concentration, particle size, and reaction temperature were kept constant at 4.0 M, $-0.20 +$

0.10 mm, and 70 °C, respectively. The variation of Mg conversion ratio with the leaching time for solid-to-liquid ratio is presented in Figure 7. It is obvious that an increase of the

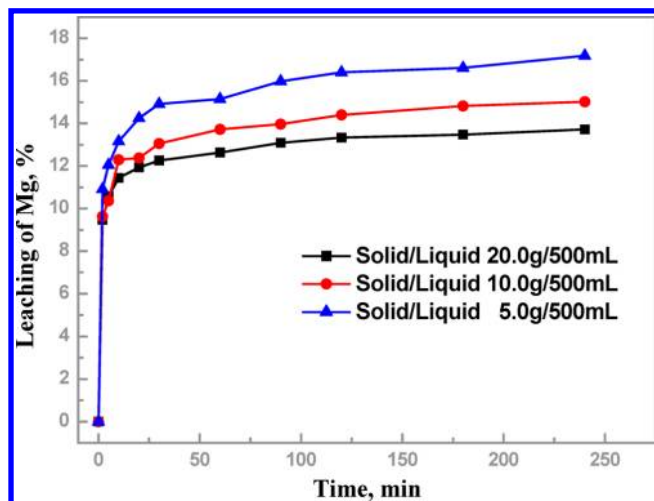


Figure 7. Effect of solid-to-liquid ratio on magnesium dissolution from calcined serpentine.

solid-to-liquid ratio from 5/500 to 20/500 g/mL, at constant reaction conditions, will decrease the conversion ratio of magnesium from 17.19% to 13.72% at the leaching time of 240 min. This can be explained by the decrease in the amount of leaching reactant per unit amount of the roasted serpentine particle with increasing of the solid-to-liquid ratio. That is, serpentine particles have more opportunity to react with the surrounding H^+ ion generated from NH_4Cl solution. Therefore, the solid-to-liquid has a counteractive effect on the extraction of magnesium.

4.7. Effect of Leaching Temperature. The reaction temperature is an important parameter in magnesium leaching. To study the effects of the reaction temperature on the extraction of Mg, a jacketed glass reactor was used at reaction temperature 70 and 104 °C (boiling point), and a high-pressure autoclave was adopted at reaction temperature of 150 °C. The initial concentration of NH_4Cl solution, particle size, and solid-to-liquid ratio, were kept constant at 4.0 M, $-0.20 + 0.10$ mm, and 20/500 g/mL, respectively. It is clear that higher reaction temperature has a greater positive effect on magnesium extraction in initial 10 min of the leaching process from Figure 8. However, in the later stage of leaching test at 150 °C, the extraction of Mg was gradually decreased with an increase of reaction time to 240 min. This result may be attributed to the accumulation of NH_3 generated from the leaching process in the high-pressure autoclave. With the increasing of NH_3 concentration, the increment of reaction solution pH stalls the reaction progress and results in a low Mg conversion. Also, the ineffective removal of NH_3 produced at temperature 70 and 104 °C in jacketed glass reactor enables the Mg extraction become gradual increased in the later reaction time (10–240 min). It is concluded that the NH_3 separation from the reaction system plays an extremely important role in Mg extraction from serpentine. According to the phase equilibria of the NH_3-H_2O system³⁵ over the temperature range from 25 to 90 °C, the solubility of $NH_3(g)$ in water decreases sharply with an increase of temperature, and 50 °C is suitable for NH_3 separation from

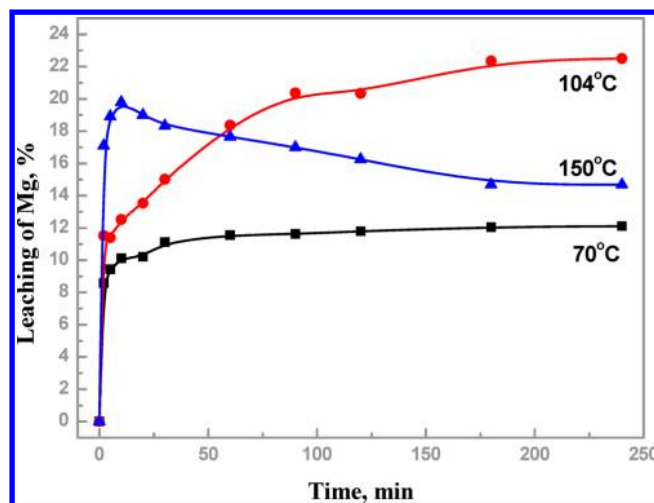


Figure 8. Effect of reaction temperature on magnesium dissolution from calcined serpentine.

water. Therefore, the temperature of circulating water in condenser pipe was kept at 50 °C in the later leaching tests.

4.8. Batch Leaching with NH_3 Removal. The extraction of magnesium from calcined serpentine was performed through single-factor investigation. However, the Mg^{2+} concentration of leaching liquid was dilute ($\sim 0.05 \text{ mol}\cdot\text{L}^{-1}$), which cannot satisfy the requirement of $Mg(OH)_2$ precipitation ($>0.5 \text{ mol}\cdot\text{L}^{-1}$). To achieve this goal, the batch leaching with NH_3 removal was carried on at a higher solid-to-liquid ratio and longer reaction time. According to the single-factor investigation, the batch leaching experiment was carried out at a higher solid-to-liquid ratio of 150/500 g/mL and longer leaching time, with roasting temperature of 700 °C, roasting time of 2 h, particle size of $-0.20 + 0.10$ mm, initial ammonium chloride concentration of 4.0 M, reaction temperature of 104 °C, and the temperature of circulating water in condenser pipe was kept at 50 °C. Nevertheless, the concentration of NH_4Cl solution was kept at about 4.0 M by adding enough solid NH_4Cl to the solution. Figure 9 presents the Mg^{2+} concentration versus the leaching time. It is obvious that the concentration of Mg^{2+} increases gradually with the reaction time (~ 20 h) to $0.63 \text{ mol}\cdot\text{L}^{-1}$, and the conversion of

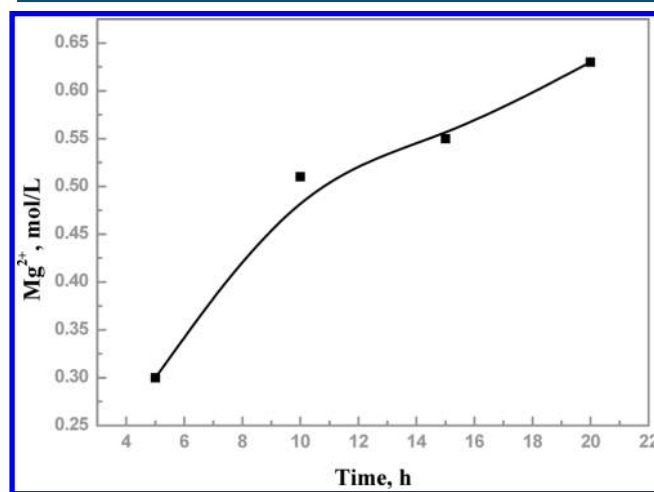


Figure 9. Mg^{2+} concentration versus the leaching time in batch experiments.

magnesium can reach 83.87%, which satisfied the demand of $\text{Mg}(\text{OH})_2$ precipitation. The XRD patterns and SEM images of raw, calcined, and leached serpentine are shown in Figures 10

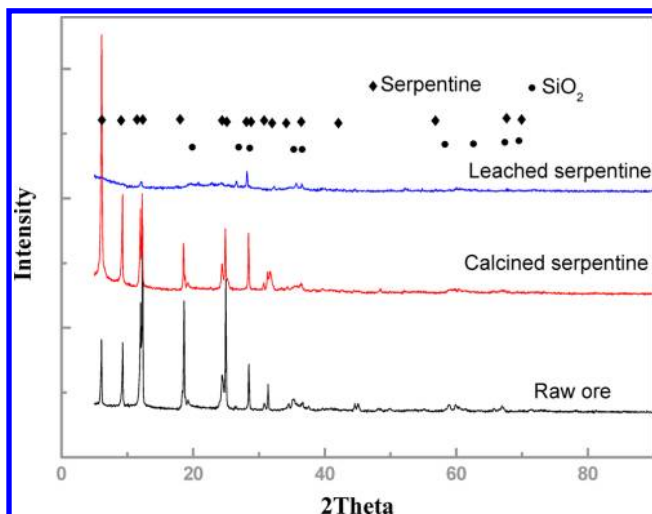


Figure 10. XRD patterns of raw, calcined, and leached serpentine, respectively.

and 11, respectively. The XRD analysis indicates that the leached serpentine were mainly SiO_2 mixed with unreacted $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$. It can be seen that needle-like particles were found in the raw and calcined serpentine (Figure 11a,b), while the leached ore are composed by the plate-shaped particles and the needle-like particles with a more or less circular contour (Figure 11c).

The mass balances for the main components were calculated. For a plant producing 10 000 tons per year of MgO (net), the mass of required serpentine and NH_4Cl would be 25 615 and 26 745 tons, respectively. Meanwhile, the amount of generated NH_3 can be reached about 8 500 tons.

4.9. Leaching Process Kinetic Analysis. The leaching process kinetic experiments for magnesium extraction were performed in condition of roasting temperature of 700°C , particle size of $-0.20 + 0.10$ mm, initial ammonium chloride concentration of 4.0 M, reaction temperature of $50\text{--}90^\circ\text{C}$, and solid-to-liquid ratio of $5/500\text{--}20/500$ g/mL. The experimental kinetic data under various conditions was correlated by the film diffusion model (eq 3), product layer diffusion model (eq 4), and chemical reaction controls model (eq 5). The analysis results showed that the experimental data fitted well to eq 4 (see Figures 12–15 and Table 2), indicating that the dissolution of calcined serpentine in NH_4Cl solution is controlled by the product layer diffusion step. This was proven by the graphical and statistical methods applied in the calculation. From the slopes of the straight lines in Figures 12–15, the values of the apparent rate constants and regression coefficients are obtained and shown in Table 2.

The activation energy of the dissolution reaction was calculated from the Arrhenius equation:

$$k = k_0 \exp\left(\frac{-E}{RT}\right) \quad (6)$$

The values of k_0 and E can be calculated from the intercept and slope of the plot of $\ln k$ against T^{-1} , and the E was calculated to be 23.56 ± 1.06 $\text{kJ}\cdot\text{mol}^{-1}$ ($R^2=0.9548$).

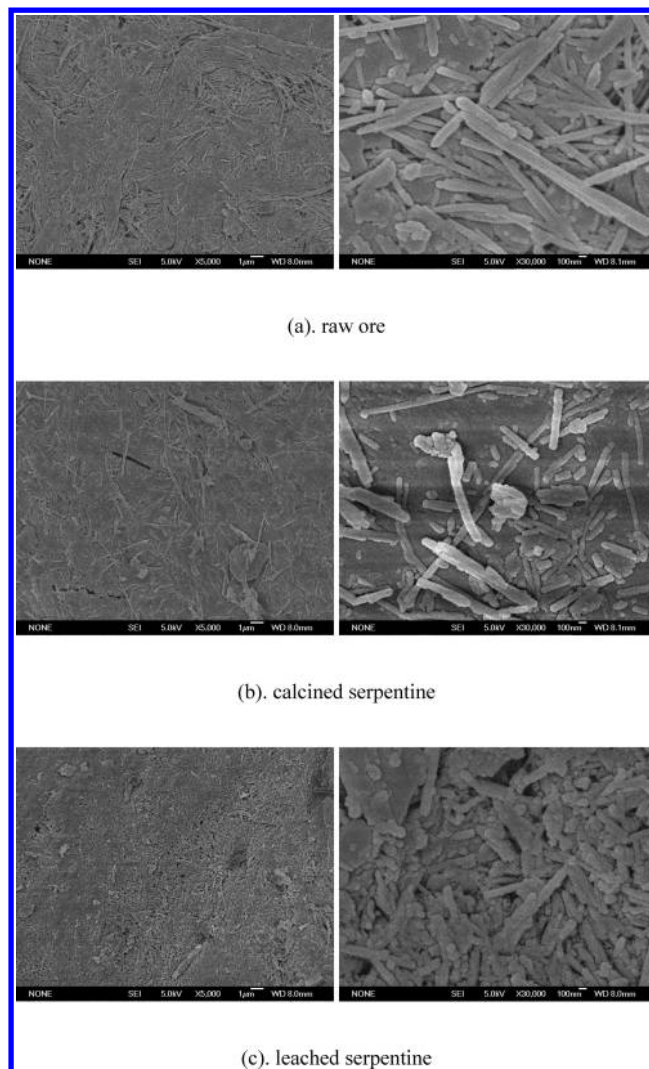


Figure 11. SEM images of raw, calcined, and leached serpentine, respectively.

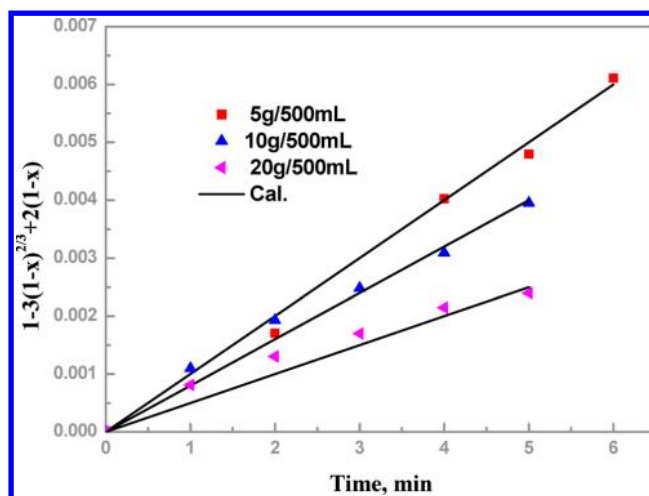


Figure 12. Variation of $1 - 3(1 - X_{\text{Mg}})^{2/3} + 2(1 - X_{\text{Mg}})$ with time for different solid-to-liquid ratio.

In order to explain the effects of the parameters on the rate constant of reaction, a semiempirical kinetic relation is also

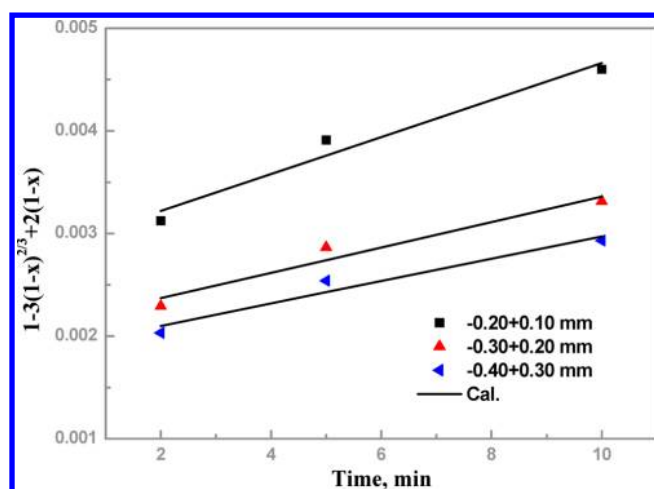


Figure 13. Variation of $1 - 3(1 - X_{Mg})^{2/3} + 2(1 - X_{Mg})$ with time for different fractions size.

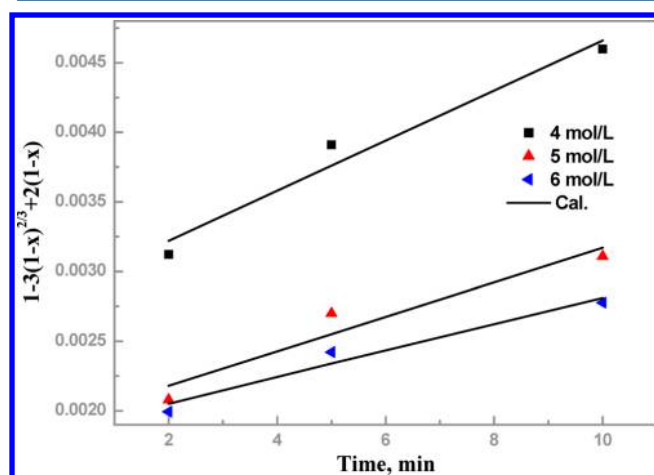


Figure 14. Variation of $1 - 3(1 - X_{Mg})^{2/3} + 2(1 - X_{Mg})$ with time for different ammonium chloride concentration.

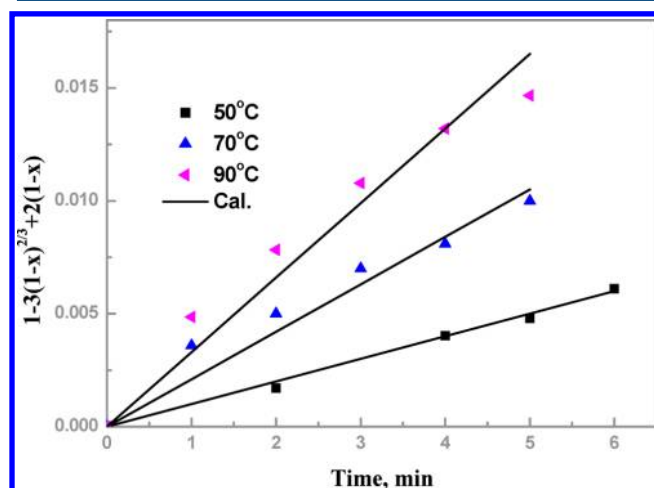


Figure 15. Variation of $1 - 3(1 - X_{Mg})^{2/3} + 2(1 - X_{Mg})$ with time for different reaction temperature.

developed to correlate experimental data for the leaching process:³⁶

$$k_2 = k_0 C_{NH_4Cl}^a d_p^b (S/L)^c \exp(-E/RT) \quad (7)$$

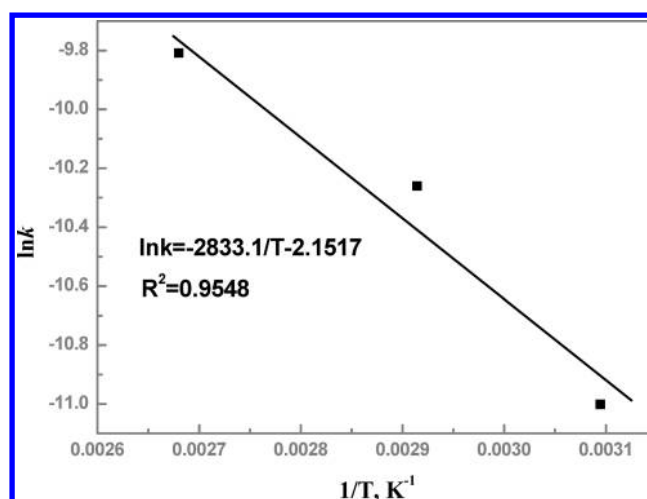


Figure 16. Napierian logarithm of reaction rate constant versus the reciprocal of absolute temperature.

Table 2. Apparent Rate Constant (k) of Magnesium and Correlation Coefficients

	k_2 (min^{-1})	$\ln(k_2)$	R^2
temp, °C			
50	9.89×10^{-4}	-6.9188	0.9945
70	2.13×10^{-3}	-6.1516	0.9421
90	3.25×10^{-3}	-5.7291	0.9472
conc, M			
4.0	1.80×10^{-4}	-8.6226	0.9673
5.0	1.24×10^{-4}	-8.9952	0.9332
6.0	9.51×10^{-5}	-9.2606	0.9619
particle size, mm			
-0.20 + 0.10	1.80×10^{-4}	-8.6226	0.9673
-0.30 + 0.20	1.24×10^{-4}	-8.9952	0.9552
-0.40 + 0.30	1.09×10^{-4}	-9.1242	0.9524
solid-to-liquid ratio, g/mL			
5/500	9.89×10^{-4}	-6.9188	0.9945
10/500	8.10×10^{-4}	-7.1185	0.9786
20/500	5.29×10^{-4}	-7.5445	0.9457

where C is the concentration of ammonium chloride, d_p is the particle size of calcined serpentine, S/L is the solid-to-liquid ratio, and a , b , and c are the parameters of the above model. By combining eq 4 with eq 7, the expression can be written as follows:

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = k_0 C_{NH_4Cl}^a d_p^b (S/L)^c \exp(-E/RT) t \quad (8)$$

Parameter estimates obtained by multiple linear regression analysis of the main reaction data of magnesium gave the correlation:

$$1 - 3(1 - x)^{2/3} + 2(1 - x) = 0.12 C_{NH_4Cl}^{-1.58} d_p^{-0.57} (S/L)^{-0.45} \exp(-23560/RT) t \quad (9)$$

From eq 9, the exponents of ammonium chloride concentration, particle size, and solid-to-liquid ratio are -1.58, -0.57, and -0.45, respectively. It is observed that eq 9 was not consistent with eq 4, which is mainly attributed to the empirical nature of eq 9. The decreasing dissolution rate with increasing NH_4Cl concentration yields a negative order of

CNH_4Cl . By empirical calculation, the order of particle diameter was obtained as a fractional order, which was similar to that reported by Gharabaghi et al.³⁷ The leaching kinetics correlation indicates that the lower concentration of ammonium chloride, smaller particle size, and lower solid-to-liquid ratio lead to higher extraction of Mg from calcined serpentine.

5. CONCLUSIONS

A process of extracting magnesium from serpentine to produce Mg compounds by using recyclable NH_3 was proposed in this work. The dissolution kinetics of magnesium from calcined serpentine in NH_4Cl solutions was investigated. An optimum condition was obtained by examining the effects of roasting temperature and time, particle size of serpentine, concentration of NH_4Cl solution, solid-to-liquid ratio, and leaching temperature on the magnesium dissolution. The optimum condition for magnesium extraction from calcined serpentine is a roasting temperature of 700 °C, roasting time of 1 h, particle size fraction of $-0.20 + 0.10$ mm, ammonium chloride concentration of 4.0 M, solid-to-liquid ratio of 20/500 g/mL, and reaction temperature of 104 °C. The maximum conversion of magnesium can reach 83.87%, and the concentration of magnesium was $\sim 0.63 \text{ mol}\cdot\text{L}^{-1}$ in batch leaching with removal of NH_3 . The reaction kinetics of the system at the studied conditions was successfully modeled by an empirical diffusion-like equation. The apparent activity energy was calculated to be $23.56 \pm 1.06 \text{ kJ}\cdot\text{mol}^{-1}$.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are grateful for the support of the Qinghai Honfoo Mining Co. LTD, the National Natural Science Foundation of China (Grant Nos. 21146006 and 21206165), and the National Basic Research Development Program of China (973 Program with Grant No. 2013CB632605).

NOTATION

- a = parameter of eq 9
- b = parameter of eq 9
- c = the concentration of ion in solution; parameter of eq 9
- C = concentration
- D_{eff} = diffusion coefficient in product layer
- m = the weight of the sample
- M = the molecular weight
- R = the radius of particle
- t = the reaction time
- V = the volume of solution
- x = the element content in sample
- X = the conversion ratio
- ρ = the density of serpentine

Subscripts and Superscripts

- i = species
- k = the kinetic constant

REFERENCES

- (1) Li, W. J.; Huang, Z. H.; Liu, Y. G.; Fang, M. H.; Ouyang, X.; Huang, S. F. Phase behavior of serpentine mineral by carbothermal reduction nitridation. *Appl. Clay Sci.* **2012**, *57*, 86–90.
- (2) Alexander, E. B. Varieties of ultramafic soil formation, plant cover and productivity. In *Ultramafic rocks: Their soils, vegetation and fauna*. Proceedings of the 4th international conference on serpentine ecology. Boyd, R. S., Baker, A. J. M., Proctor, J., Eds.; Science Reviews, St. Albans: Herts, U.K., 2004; pp 9–17.
- (3) Lee, B. D.; Graham, R. C.; Laurent, T. E.; Amrhein, C. Pedogenesis in a wetland meadow and surrounding serpentinitic landslide terrain, northern California, USA. *Geoderma* **2004**, *118*, 303–320.
- (4) Kierczak, J.; Neel, C.; Bril, H.; Puziewicz, J. Effect of mineralogy and pedoclimatic variations on Ni and Cr distribution in serpentine soils under temperature climate. *Geoderma* **2007**, *142*, 165–177.
- (5) Lackner, K. S.; Butt, D. P.; Wendt, C. H. Magnesite disposal of carbon dioxide. In *Proceedings of the 22nd International Technical Conference on Coal Utilization and Fuel Systems*, Clearwater, Florida, 1997; pp 419–430.
- (6) Auzende, A. L.; Daniel, I.; Reynard, B.; Lemaire, C.; Guyot, F. High-pressure behaviour of serpentine minerals: a Raman spectroscopic study. *Phys. Chem. Miner.* **2004**, *31*, 269–277.
- (7) Cheng, T. W.; Ding, Y. C.; Chiu, J. P. A study of synthetic forsterite refractory materials using waste serpentine cutting. *Miner. Eng.* **2002**, *15*, 271–275.
- (8) Pietrikova, A.; Bugel, M.; Golja, M. Preparation of SiO_2 powder through leaching of serpentine. *Metallurgija* **2004**, *43*, 299–304.
- (9) Kanari, N.; Menad, N.; Gaballag, I. Some aspects of the reactivity of olivine and serpentine towards different chlorinating gas mixtures. *Thermochim. Acta* **1998**, *319*, 97–104.
- (10) Cheng, T. W.; Hsu, C. W. A study of silicon carbide synthesis from waste serpentine. *Chemosphere* **2006**, *64*, 510–514.
- (11) Wang, X.; Maroto-Valer, M. M. Dissolution of serpentine using recyclable ammonium salts for CO_2 mineral carbonation. *Fuel* **2011**, *90*, 1229–1237.
- (12) Zhang, Z.; Lu, X.; Yang, S.; Pan, F. Preparation of anhydrous magnesium chloride from magnesite. *Ind. Eng. Chem. Res.* **2013**, *51*, 9713–9718.
- (13) Li Z. B.; Wang, J. F. Method of preparing anhydrous magnesium chloride for electrolysis magnesium using ionic liquids by solar energy. CN Patent 201010108988, 2010.
- (14) Hoşgün, H. L.; Kurama, H. Dissolution kinetics of magnesite waste in HCl solution. *Ind. Eng. Chem. Res.* **2012**, *51*, 1087–1092.
- (15) Wang, D. G.; Li, Z. B. Modeling solid-liquid equilibrium of NH_4Cl - MgCl_2 - H_2O system and its application to recovery of NH_4Cl in MgO production. *AIChE J.* **2011**, *57*, 1595–1606.
- (16) Gao, W. C.; Li, Z. B. A practical approach to produce Mg-Al spinel based on the modeling of phase equilibria for NH_4Cl - MgCl_2 - AlCl_3 system. *AIChE J.* **2013**, *59*, 1855–1867.
- (17) MacIntire, W. H. Process for producing anhydrous magnesium sulphate. U.S. Patent 2298493, 1942.
- (18) Kosuge, K.; Shimada, K.; Tsunashima, A. Micropore formation by acid treatment of antigorite. *Chem. Mater.* **1995**, *7*, 2241–6.
- (19) Alexander, G.; Maroto-Valer, M. M.; Gafarova-Aksoy, P. Evaluation of variables in the dissolution of serpentine for mineral carbonation. *Fuel* **2007**, *86*, 273–281.
- (20) Lackner, K. S.; Wendt, C. H.; Butt, D. P.; Joyce, E. L.; Sharp, D. H. Carbondioxide disposal in carbonate minerals. *Energy* **1995**, *20*, 1153–1170.
- (21) Ficarra, P.; Chin, E.; Walker, T.; Laroche, D.; Palumbo, E.; Celik, C.; Avedesian, M. Magnolia: A novel commercial process for the primary production of magnesium. *CIM Bull.* **1998**, *91*, 75–80.
- (22) Dutrizac, J. E.; Chen, T. T.; White, C. W. Fundamentals of serpentine leaching in hydrochloric acid media. In *Magnesium Technology*; Kaplan, H., Hryn, J., Clow, B., Eds.; The Minerals, Metals & Materials Society: Nashville, TN, 2000; pp 41–51.

- (23) Teir, S.; Revitzer, H.; Eloneva, S.; Fogelholm, C.-J.; Zevenhoven, R. Dissolution of natural serpentinite in mineral and organic acid. *Int. J. Miner. Process.* **2007**, *83*, 36–46.
- (24) Park, A. H. A.; Jadhav, R.; Fan, L. S. CO₂ mineral sequestration: chemically enhanced aqueous carbonation of serpentine. *Can. J. Chem. Eng.* **2003**, *81*, 885–890.
- (25) Maroto-Valer, M. M.; Fauth, D. J.; Kuchta, M. E.; Zhang, Y.; Andrésen, J. M. Activation of magnesium rich minerals as carbonation feedstock materials for CO₂ sequestration. *Fuel Process. Technol.* **2005**, *86*, 1627–45.
- (26) Kim, D.; Sohn, J.; Ahn, J.; Chung, H. Extraction of metals from mechanically milled serpentine. *Geosyst. Eng.* **2008**, *11*, 25–28.
- (27) Van Essendelft, D. T.; Schobert, H. H. Kinetics of the acid digestion of serpentine with concurrent grinding. 1. Initial investigations. *Ind. Eng. Chem. Res.* **2009**, *48*, 2556–2565.
- (28) Van Essendelft, D. T.; Schobert, H. H. Kinetics of the acid digestion of serpentine with concurrent grinding. 2. Detailed investigation and model development. *Ind. Eng. Chem. Res.* **2009**, *48*, 9892–9901.
- (29) Van Essendelft, D. T.; Schobert, H. H. Kinetics of the acid digestion of serpentine with concurrent grinding. 3. Model validation and prediction. *Ind. Eng. Chem. Res.* **2010**, *49*, 1588–1590.
- (30) Zhang, Q.; Sugiyama, K.; Saito, F. Enhancement of acid extraction of magnesium and silicon from serpentine by mechanochemical treatment. *Hydrometallurgy* **1997**, *45*, 323–331.
- (31) Fedorocková, A.; Hreus, M.; Raschman, P.; Sucik, G. Dissolution of magnesium from calcined serpentinite in hydrochloric acid. *Miner. Eng.* **2012**, *32*, 1–4.
- (32) Pundsack, F. L.; Somerville, N. J. Recovery of silica, iron oxide and magnesium carbonate from the treatment of serpentine with ammonium bisulphate. U.S. Patent 3338667, 1967.
- (33) Wang, X.; Maroto-Valer, M. M. Dissolution of serpentine using recyclable ammonium salts for CO₂ mineral carbonation. *Fuel* **2011**, *90*, 1229–1237.
- (34) Levenspiel, O. *Chemical Reaction Engineering*, 2nd ed.; John Wiley and Sons: New York, 1972.
- (35) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 89th ed.; Boca Raton: CRC Press, 2009.
- (36) Demirkiran, N. A study on dissolution of ulexite in ammonium acetate solutions. *Chem. Eng. J.* **2008**, *141*, 180–186.
- (37) Gharabaghi, M.; Irannajad, M.; Azadmehr, A. R. Leaching behavior of cadmium from hazardous waste. *Sep. Purif. Technol.* **2012**, *86*, 9–18.