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# Magnesium Chloride Crystals with Studying Mechanism and Leaching Kinetics of Serpentinite Ore by Hydrochloric Acid

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Abstract Magnesium chloride hexahydrate crystal (MgCl<sub>2</sub>.6H<sub>2</sub>O) is an intermediate product used to obtain Mg metal from its ores. This work aims to produce purified MgCl<sub>2</sub>.6H<sub>2</sub>O crystals from natural Egyptian serpentine. Serpentine samples were collected from the Eastern Desert in Egypt and prepared for leaching with HCl solutions. Reaction temperature (°C), leaching time (h), solid/liquid ratio (g/mL), and acid concentration (M) were studied. The optimum leaching conditions achieved 97.6% MgO recovery optimized at particle size less than 75 µm (100%), 95 °C of the reaction temperature for three hours with solid-to-liquid ratio 1:5, and 5 M of HCl concentration. The serpentine dissolution kinetics were studied depending on the solid-liquid reaction and activation energy model. The resultant liquor was purified and crystallized. The kinetic studies indicated that product layer diffusion is the most likely rate-controlling step for serpentinite dissolution in the HCl solution.

**Keywords** Serpentine · Magnesium chloride hexahydrate · Dissolution kinetics

# **1** Introduction

The global demand for Mg metal was estimated at USD 3.5 billion in 2019 and is expected to reach USD 3.81 billion by 2027 [1]. Mg metal has become a highly demanded metal in automotive and structural applications to save energy

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<sup>2</sup> Chemistry department, Faculty of Science, Ain Shams University, Cairo, Egypt consumption and reduce pollution. Serpentinite is a type of rock that contains one or more serpentine group minerals. Antigorite, chrysotile, and lizardite are three hydrated magnesium silicate minerals constituting serpentinite rock. They all have the same chemical formula  $[(Mg)_3Si_2O_5(OH)_4]$  but different crystal structures [2]. It typically contains 32–38% magnesium oxide and 35–40% with minor amounts of Fe, Al, Ca, Cr, and Ni [3]. The serpentine mineral is found all over the world. The world's most significant serpentine ores commercial resources are in Canada, Russia, and Africa [4]. Furthermore, serpentine ores are found in Egypt, especially in the Eastern Desert [5–8].

In addition to utilizing serpentines as one of the natural mineral resources of Mg metals, it is also used as railway ballasts, construction materials, and electrical insulation. Furthermore, large serpentinite reserves could be used in more advanced applications such as carbon dioxide capturing and storage [9], as a magnesium source [10, 11], and as a raw material in the production of magnesium compounds. The most common salt derivatives of magnesium that can be extracted from serpentine are magnesium sulfate, magnesium chloride, magnesium hydroxide, magnesium oxide, and magnesium which can be used in magnesium metal production, textiles, pharmaceuticals, ceramics, cement, paper processing, fertilizers, and chemical treatment [8].

Acid leaching of serpentine is usually the first stage of the overall process in the synthesis of pure magnesium compounds. After leaching, the soluble magnesium chloride salt is separated from the insoluble residue and purified [2]. Commonly used lixiviants are hydrochloric acid [12–14], sulfuric acid [3, 8], and other inorganic and organic acids. Several investigations into serpentinite rock have been done to understand its dissolution characteristics better. Singh et al. investigated the effect of solvent concentration, sample size, reaction temperature, and reaction time

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on Mg extraction that was explored using three acids: HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>. The activation energy was calculated for the dissolution kinetics of Mg, which follows the product layer diffusion process with 17.45 kJ·mol<sup>-1</sup>(0–30 min) and 14.12 kJ·mol<sup>-1</sup>(60–120 min) [15]. Abou El-Leef et al. investigated the best conditions for leaching Mg<sup>2+</sup> ions from serpentine ore using sulfuric acid. They found that the rate of magnesia dissolution in H<sub>2</sub>SO<sub>4</sub> acid solutions was regulated by a chemical reaction on the surface of the serpentine ore particle [8]. Yoo et al. used  $H_2SO_4$  to explore the dissolution mechanism of ground serpentine. They found that diffusion through tiny channels formed between the silica layers in serpentine particles appears to control the rate of Mg dissolution and that they achieved complete dissolution of Mg from natural serpentine in 0.5 h at 90 °C using 0.5 M H<sub>2</sub>SO<sub>4</sub> [3]. Wang and Mercedes Maroto-Valer investigated serpentine dissolution using ammonium salts. They demonstrated that at 100 °C, 1.4 M NH<sub>4</sub>HSO<sub>4</sub> solution could extract 100% Mg from serpentine in 3 h [16, 17]. Maroto-Valer et al. used physical and chemical activation to activate the mineral before dissolution [18]. Fagerlund et al. investigated this process in detail and proposed a way to obtain value-added products by leaching at various pressures [19]. Mucha et al. presented a shrinking core model to explain serpentinite dissolution in acid [20]. Park and Fan examined physically activated serpentine dissolution and the pH swing method for using serpentine rocks for  $CO_2$  sequestration [21].

Several studies on Egyptian serpentine ore have been done, including thermal analysis [5], location in Egypt [6], and mineralogical studies [7]. So far, no studies have been focused on the fundamental and industrial chemical leaching of Egyptian serpentinite rocks as a feedstock source for magnesium compounds and producing purified MgCl<sub>2</sub>.6H<sub>2</sub>O crystals as an intermediate product for the Mg metal industry in the electrolytic process.

Therefore, this work aims to determine the optimum conditions for dissolving serpentine minerals in an HCl solution to produce magnesium chloride. We investigated the effects of HCl content, dissolution temperature, reaction time, and solid/liquid ratio on the dissolution of Mg. Furthermore, the Mg dissolution kinetics reported in this research was obtained by reducing the effects of film boundary diffusion and particle size.

#### 2 Methods

# 2.1 Materials and Chemicals

A batch of 5 kg serpentinite rock from the Eastern Desert (Egypt) was ground to a particle size 100% less than 75  $\mu$ m. Chemicals with an analytical grade of HCl (ADWIC, 36%),

 $H_2SO_4$  (ADWIC, 98%), ammonia (ADWIC, 33%), and deionized water were used in all experiments.

# 2.2 Characterization of Serpentinite Rock Sample

A Bruker AXS diffractometer (D8-ADVANCE) with Cu K radiation, operating at 40 kV and 10 mA, was used to characterize the serpentine sample. The scanning rate was 0.5°min<sup>-1</sup>, and diffraction data for 20 values ranging from 4° to 70° were collected. The X-ray powder data file, released by the American Standard for Testing Material (ASTM), was used to identify the phases in the samples. For sample imaging, a JEOL model JSM-5410 scanning electron microscope was employed. The chemical composition of the rock was determined using a Philips X-ray fluorescence (XRF) spectrometer.

# 2.3 Leaching Experiments

During constant agitation, the calculated amount of serpentine was progressively added to the HCl solution in the reaction flask. The reaction took place in a 500 mL roundbottom flask immersed in a water bath and was set to the desired temperature. The reaction mixture was agitated at a speed of 500 r.p.m. The variables studied included leaching temperature, time, S:L ratio, and molarity, and the leaching efficiency was calculated. The applied variables were leaching temperature (35, 55, 75, 95, and 98 °C), leaching time (1, 2, 3, and 4 h), solid/liquid ratio (1:3, 1:5, 1:10, 1:20), and molarity (1, 3, 5, and 7 M). After the desired reaction time, the slurry was treated with a calculated amount of sulfuric acid to precipitate calcium, then neutralized to pH 7.0–7.5, and then filtered under vacuum in a Buchner-type filter using polypropylene filter cloth of 200 mesh aperture size and the residue was washed two times. The residue contains silica, calcium sulfate, ferric hydroxide, and other impurities. The filtrate was analyzed for MgO and CaO contents, followed by evaporation to crystallization. The total MgO content of the resulting crystals was determined.

The accumulated MgO recovery (recovery, %) during the leaching step was determined by withdrawing 10 mL using a filter syringe at different time intervals. The percentage of MgO recovery from the ore during leaching was calculated according to the following equation:

Recovery (%) = 
$$\frac{W_f}{W_i} \times 100$$

where  $W_f$  is the determined weight of MgO in the leaching solution and  $W_i$  is the weight of MgO in the initial sample.

This equation helps determine the fraction of MgO extracted during leaching step, followed by determining the rate constant and activation energy of dissolution to understand the mechanism of serpentine leaching with HCl [8].

#### 2.4 Dissolution Kinetics of Serpentinite

At the required temperature, 10 gm of ground serpentine ore was added to a 1000 ml agitated HCl solution at a concentration of 5 M. At the selected time intervals (1, 3, 5, 10, 15, 30, 60, 90, 120, 150, and 180 min), using a filter syringe with a one  $\mu$ m pore size, a 2 ml solution sample was obtained, and the solids matching that volume were discarded. As a result, the solid-to-liquid ratio was kept at 1: 100. When compared to the initial solution, the cumulative volume eliminated by sampling was negligible(~ 2%). Evaporated water was continually adjusted. The concentration of MgO in the samples was determined, and the percent extraction of MgO was calculated.

# **3** Results and Discussion

# 3.1 Phase Composition and Chemical Composition of Serpentine

The XRD analysis of the serpentine mineral specimen is shown in Fig. 1. It shows that the major mineral is antigorite  $[Mg_3Si_2O_5(OH)_4]$ . Applying XRF analysis on the serpentine sample, the chemical composition of the ore is shown in Table 1. The serpentine sample is characterized by high contents of MgO and SiO<sub>2</sub>, low CaO, and low Al<sub>2</sub>O<sub>3</sub>, as shown in Table 1. Moreover, considerable quantities of NiO and Cr<sub>2</sub>O<sub>3</sub> are also present in the composition of the serpentine ore sample.



Fig. 1 XRD pattern of serpentine mineral (↓ Antigorite)

Component	Concentration, %	Component	Concentration, %
SiO <sub>2</sub>	36.80	MnO	0.163
MgO	35.82	ZnO	0.091
Fe <sub>2</sub> O <sub>3</sub>	7.64	SO <sub>3</sub>	0.031
Cao	3.81	$Co_3O_4$	0.026
NiO	0.44	SrO	0.015
$Al_2O_3$	0.38	$P_2O_5$	0.008
Cr <sub>2</sub> O <sub>3</sub>	0.36	CuO	0.007

Loss on ignition at 1000 °C is 14.4%

#### 3.2 Leaching of Serpentine Mineral

HCl was used to investigate the possibility of  $Mg^{2+}$  ions being leached from serpentine material. Leaching is based on the decomposition of the mineral with HCl. The quantities of reactants were calculated stoichiometrically using the following equation:

$$Mg_{3}Si_{2}O_{5}(OH)_{4} + 6HCl \rightarrow 3MgCl_{2} + 2SiO_{2} + 5H_{2}O$$
(2)

Hydrochloric acid reacts with some impurities according to the following equations:

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O$$
(3)

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O$$
 (4)

#### 3.2.1 Effect of Reaction Temperature

Experiments were carried out at temperatures ranging from 35 to 98 °C. The following conditions were used to study the effect of the temperature on MgO recovery by leaching with aqueous HCl solution: Reaction time is 1 h, solid-to-liquid ratio is 1:5 g/ml, and acid concentration is 5 M. The results are shown in Fig. 2a, which reveal that MgO recovery increases as temperature increases. The optimum temperature is 95 °C, which results in a MgO recovery of 86.5%.

# 3.2.2 Effect of Reaction Time

The reaction time effect was studied at different time periods (1-4 h), where temperature, solid/liquid ratio, and acid concentration were set at 95 °C, 1:5 g/mL, and 5 M to optimize the recovery of MgO at the optimum reaction time. Figure 2b shows that the interaction of serpentine with hydrochloric acid is a high-rate spontaneous reaction. Increasing MgO recovery causes increased reaction time due to the magnesium cations trapped in cavities of serpentine



Fig. 2 Effect of leaching parameters on MgO recovery: Reaction temperature (a), Reaction time (b), Solid/liquid ratio (c), and Hydrochloric acid concentration (d)

ore easily liberated to the solution. The optimum recovery of MgO, 97.4%, was obtained after 3 h of reaction time, while extending the time of reaction to more than 3 h did not achieve a notable increment in MgO recovery. So, the optimum fitted reaction time is considered after 3 h.

# 3.2.3 Effect of Solid-to-Liquid Ratio

The solid-to-liquid ratios were studied with a range starting from 1:3 to 1:20 g/ml to investigate the influence of the solid-to-liquid ratio on MgO recovery. The mole ratio of MgO to HCL was kept at a constant value while changing the ratios of solid (ore) and liquid (solution) by adopting the HCl concentration. Figure 2c indicates that a higher solidto-liquid ratio (1:20) results in a lower magnesium chloride concentration (83.4%) because of the decreased corresponding acid concentration. The low concentration of magnesium salts resulting from the increasing solid-to-liquid ratio leads to intensive energy consumption during the evaporation and crystallization step in the magnesium salt production process. At a higher solid-to-liquid ratio, the magnesium salt concentration is low, which needs higher energy for evaporation in the crystallization step during the production process of magnesium salt. Meanwhile, at a lower solid-to-liquid ratio, the magnesium salt concentration is high due to the highly saturated magnesium solution that easily crystallizes leading to losses of MgO salts during filtration. Furthermore, due to the high viscosity of the solution, the filtration rate is quite low. The results reveal that the optimal solid-to-liquid ratio is 1:5 g/ml, yielding a 96.3% MgO recovery.

# 3.2.4 Effect of HCl Concentration

The HCl solution concentration effect was studied at different strengths ranging from 1.0 to 7.0 M, where temperature, solid/liquid ratio, and reaction time were kept at 95 °C, 1:5 g/mL, and 3 h. Experiments were carried out at the above conditions, changing the HCl solution concentration from 1.0 to 7.0 M to investigate the impact of HCl concentration on the recovery of MgO, as shown in Fig. 2d. The increase in the concentration of HCI leads to an increase in MgO recovery, which at 5 M reaches 97.6%. Any other increment in this molar ratio leads to raising H<sup>+</sup> ions in the solution, which results in more acid consumption and more chemicals for neutralizing without an appreciable increase in MgO recovery.

It was concluded that the optimum leaching conditions of Egyptian serpentine ores are particle size less than 75  $\mu$ m, reaction temperature at 95 °C for 3 h with solid/liquid ratio 1:5, and 5 M of HCl acid solution that leads to 97.6% MgO recovery.

It is worth mentioning that the reaction time required to achieve a certain degree of conversion of the magnesium is not an independent quantity, but it mainly depends on the size of the serpentinite particles and on the concentration and temperature of the acid.

#### 3.3 Kinetic Analysis

Experimental studies reveal that the Mg recovery from serpentine ores depends on the varied parameters of the applied process synchronized with its dissolving behavior. Material dissolving behavior is determined by the interaction between the acid reactant and the solid. This reaction is determined by the solid–liquid reaction model and the energy of activation.

There are mainly three methods, product layer developed on the surface of the particle, film diffusion, or chemical reaction caused by unreacted ore, controlling the solid–liquid reactions. The slowest step of these methods controls the reaction rate. The dissolution characteristics of serpentinite rocks have been studied by many researchers, as shown in Table 2. This research work conducted experiments with particle size 100%-200 mesh of the sample, 5 M acid concentration of 5 M, and at various applied temperatures in the reaction. The results of the experiments are presented in Fig. 3 for various times and temperatures. Table 3 shows the correlations for the shrinking core for spherical particles of constant size, as suggested by Teir et al. [22] and based on integral rate equations. For each correlation equation, the multiple regression coefficient ( $\mathbb{R}^2$ ) was calculated, and the rate-determining step was determined for the equation with the highest  $R^2$  value.

Based on the correlation curves plotted in Fig. 3, the product layer diffusion model fits the experimental data. It clarifies that the product layer diffusion might be the most appropriate rate-controlling step for dissolving serpentine using an HCl solution. In addition, the rate-determining mechanism for serpentine dissolving in 1.4 M NH<sub>4</sub>HSO<sub>4</sub> solution is product layer diffusion, which is reported by Wang et al. [16]. Another suggestion presented by Teir et al. is that product layer diffusion is the control mechanism since less percentage of silica is extracted into the solution[22], and also, Yang et al. suggested Mg dissolving followed the shrinking core model and the rate determined by internal diffusion [15]. Therefore, this work agrees with previous studies that the product layer diffusion model is the most appropriate rate-determining step for serpentine dissolving via hydrochloric acid solution.

From Fig. 3 c, the obtained slope was used to calculate the activation energy (E) according to the Arrhenius equation and calculate the apparent rate constant (k) as well according to the following equation:

$$K = Ae^{\frac{-E_2}{RT}}$$
(5)

where k is the apparent rate constant, T is the absolute temperature in Kelvin, A is the frequency factor,  $E_a$  is the activation energy for the reaction, and R is the universal gas constant (R = 8.314 J/molK).

The value of activation energy is determined by plotting the natural log of the apparent rate constant (ln k) against the reciprocal of the absolute temperature (1/T), as shown in Fig. 3 d, which is 44.4 kJ. Mol<sup>-1</sup>. The obtained value of activation energy with previously reported studies is shown in Table 2 [15, 16, 23]. The lower value of the obtained activation energy compared to the obtained one by Teir et al. [22] may be resulted from the applied low-temperature ranges and large particle size used in this study. Although Yoo et al. [3] used the same particle size, the obtained activation energy was 80 kJ.mol<sup>-1</sup> which was considered a high value compared to this study. However, this high value may be due to the low acid concentration used in his work. As

 Table 2
 Comparison of the dissolution data from previous work compared to the present study

$E_a(kJ.mol^{-1})$	Dissolution conditions	Particle size of serpen- tine ore	References
35.6	3 M H <sub>2</sub> SO <sub>4</sub> ,30–75 °C	100- 250 μm	Fouda et al. [23]
82	0.5 M H <sub>2</sub> SO <sub>4</sub> ,25–90 °C	<45 μm	Yoo et al. [3]
40.9	1.4 MNH <sub>4</sub> HSO <sub>4</sub> ,70–110 °C	75–150 μm	Wang et al. [16]
70	2 M HCl, 30–70 °C	74–125 μm	Teir et al. [22]
17.45	$(0.5-1.0 \text{ mL/g}) \text{ H}_2\text{SO}_4$ , roasting	NA	Singh et al. [15]
44.4	5 M HCl, 35– 95 °C	<75 μm	This work



Fig. 3 Kinetic study of Mg dissolution for: Film Diffusion controlled (a), Chemical Reaction Controlled (b), Product Layer controlled (c); and Arrhenius plot for Mg extraction for 5 M HCl (d)

Table 3Regression coefficientsrange with experimental kineticdata fitted to shrinking core

R <sup>2</sup> Range	Correlation equation	Model name
0.63577–0.73214	kt = X	Film Diffusion
0.73101-0.97937	$kt = 1 - 3(1 - X)^{2/3} + 2(1 - X)$	Product Layer Diffusion
0.64716-0.92687	$kt = 1 - (1 - X)^{1/3}$	Chemical Reaction Controlled

presented in Table 2, these studies found that the leaching of serpentine ores via hydrochloric acid has similar kinetics and follows the product layer diffusion mechanism in most of their comparable activation energy ranges.

# 3.4 Hydrated Magnesium Chloride Crystals

The preparation method of purified hydrated magnesium chloride crystals involve leaching serpentine ore with 5 M HCl solution for 3 h at 95  $^{\circ}$ C in order to produce maximum

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MgO leaching from the ore. The resultant liquor solution was purified by precipitating Ca as sulfate with a stoichiometric amount of  $H_2SO_4$ , as shown in Eq. 6[24];

$$H_2SO_4 + CaCl_2 \rightarrow CaSO_4 + 2HCl$$
(6)

After filtration, diluted ammonia was added to raise the pH to 5.5–6. to ensure the precipitation of  $Al^{3+}$ ,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Ni^{2+}$ ,  $Co^{3+}$ , and  $Cr^{3+}$  as hydroxides, then filtrate. SEM images and EDX of impurities precipitated from the purification of the resulting liquor solution to obtain a pure solution of  $MgCL_2.6 H_2O$  in Fig. 4.

The magnesium chloride solution evaporated until the specific gravity of the solution reached 1.45 g/ml. The solution was cooled, and magnesium chloride hexahydrate was crystallized [24]. The produced MgCl<sub>2</sub>· $6H_2O$  crystals were analyzed by EDX (Fig. 5). The block flow sheet for the preparation of magnesium chloride hexahydrate from serpentinite ore is illustrated in Fig. 6.

# 4 Conclusions

This study concluded the optimum leaching conditions of Egyptian serpentine ores to achieve 97.6% MgO recovery at particle size less than 75  $\mu$ m (100%), 95 °C of the reaction temperature for 3 h with solid-to-liquid ratio 1:5, and 5 M of HCl solution concentration. This study found that serpentine ore dissolution kinetics depended on the solid/liquid reaction model and activation energy. The kinetic studies proved that product layer diffusion could be the most appropriate rate-controlling step for the serpentine dissolution by HCl. This study succeeded in reaching the purified



**Fig.4** SEM image of precipitate after addition of diluted  $H_2SO_4$  (**a**) and EDX spectra of detected elements (**b**) with inserted tables of weights %. **c** and **d** are the SEM and EDX spectra of the precipitate after addition of diluted ammonia, with inserted table for weights %, respectively



Fig.5 SEM image of purified MgCL<sub>2</sub>.6H<sub>2</sub>O crystals (a), and EDX spectra of detected elements (b) with inserted tables of weights %



Fig. 6 Block flow diagram for preparation of magnesium chloride hexahydrate from serpentine ore

MgCl<sub>2</sub> solution, followed by evaporation and crystallization to obtain MgCl<sub>2</sub>.6H<sub>2</sub>O crystals.

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