

Research Article

An Analytical Model Approach for the Dissolution Kinetics of Magnesite Ore Using Ascorbic Acid as Leaching Agent

Nadeem Raza, Zafar Iqbal Zafar, and Najam-ul-Haq

Institute of Chemical Sciences, Bahauddin Zakariya University, Multan 60800, Pakistan

Correspondence should be addressed to Nadeem Raza; nadeemr8@hotmail.com

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Ascorbic acid was used as leaching agent to investigate the dissolution kinetics of natural magnesite ore. The effects of various reaction parameters such as acid concentration, liquid-solid ratio, particle size, stirring speed, and temperature were determined on dissolution kinetics of the magnesite ore. It was found that the dissolution rate increased with increase in acid concentration, liquid-solid ratio, stirring speed, and temperature and decrease in the particle size of the ore. The graphical and statistical methods were applied to analyze the kinetic data, and it was evaluated that the leaching process was controlled by the chemical reaction, that is, $1 - (1 - x)^{1/3} = 1.256 \times 10^5 e^{-57244/RT} t$. The activation energy of the leaching process was found to be $57.244 \text{ kJ mol}^{-1}$ over the reaction temperature range from 313 to 343 K.

1. Introduction

Magnesium is the third most commonly used structural metal after iron and aluminum. The applications of magnesium involve aerospace, automobiles, flash photography, flares, pyrotechnics, Grignard reagent, refractory materials, food, fertilizers, medicinal products, paper, textile, alloy formation, to remove sulfur in the production of iron and steel, fireproof, and so forth as described by Jones et al. [1].

With increase in population, there is continuous increase in demand of magnesium and its compounds. To overcome the increasing demand of magnesium and its compounds there is a need to explore ores of magnesium (magnesite, dolomite, etc.). These ores may vary in composition from deposit to deposit resulting differences in acidulation processes. These rocks generally contain impurities such as calcium, iron, and silica which can cause adverse effects on the applications of magnesium and its compounds.

The leaching and dissolution studies of different ores with different leaching agents are available in the literature [2–11]. On industrial scales different leaching agents are used to leach ores of various compositions to get different metals and their compounds. Inorganic/organic acids or bases and their salts can be used for leaching of magnesite rocks to get magnesium

and its compounds. From the dissolution studies of magnesite rocks by inorganic acids such as HCl, H_2SO_4 , it was found that the dissolution reaction was chemically controlled [12, 13]. The inorganic acids are regarded as good leaching agents when relatively fast reaction rates are required. However, the use of inorganic acids as leaching agents affords certain limitations, like less selectivity, scaling problems, high CO_2 pressure, corrosion, environmental problems, froth formation, and pH control of reaction medium [14]. On contrary to inorganic acids, organic acids may be more selective as compared to inorganic acids and can be used for dissolution of specific ores where relatively low-acid concentrations are favorable. The reaction mediums involving organic acids as leaching agents have various advantages like low risk of corrosion and froth accumulation and biodegradability of organic acids. Furthermore, their corrosion effect can be reduced by the addition of corrosion inhibitors such as benzoic acid and salicylic acid [15]. However, organic acids may have less ability to leach some ores at higher temperatures due to their low boiling points and decomposition problems. The leaching kinetics of low-grade phosphate rock involving dilute organic acids such as succinic acid and lactic acid was carried out [16, 17], and it was investigated that the leaching process was chemically controlled. The literature

concerning the dissolution studies of magnesite in citric acid and in gluconic acid is also available [18, 19]. In these research studies, it was evaluated that the dissolution process was controlled by chemical reaction. Lacin et al. [20, 21] carried out data analysis using shrinking core models for fluid solid systems in the dissolution kinetics study of natural magnesite in acetic acid and lactic acid solutions and found that the dissolution rate was controlled by chemical reaction.

Large deposits of magnesite are present in Khuzdar area of Balochistan (Pakistan). These deposits have different compositions from ore to ore. Studies of leaching reaction kinetics at different conditions of various reaction parameters of these deposits have not been carried out. Therefore, in the present research work indigenous magnesite ore has been taken to investigate the dissolution kinetics at different conditions of various reaction parameters.

2. Methods and Materials

2.1. Sample Preparation and Analysis. The magnesite ore used in the present research work was obtained from Khuzdar area of Balochistan (Pakistan). Khuzdar area is widely endowed with magnesite ore deposits. Samples of natural magnesite ore were collected and crushed with ball mill and mortar grinder. ASTM standard sieves were used to obtain the desired particle size fractions. Örgül and Atalay [22] found that, when minerals are fractionated, the chemical composition of each fraction with definite particle size is usually changed. All the magnesite samples were dried in an electric oven at 100°C, cooled to room temperature, and stored in dry plastic bottles. EDX was used for the analysis of the magnesite rock fractions along with the other conventional analytical techniques [23]. Analytical results indicating the composition of magnesite ore have been shown in Tables 1 and 2. The EDX pattern indicating the elemental composition of the raw magnesite ore has been shown in Figure 1. Different chemicals used in dissolution studies of magnesite ore were of reagent grade.

The leaching agent used in this research work was ascorbic acid [(5R)-[(1S)-1,2-dihydroxyethyl]-3,4-dihydroxyfuran-2(5H)-one] commonly called vitamin C, abundantly found in citrus fruits. It is a naturally occurring organic compound with antioxidant properties. It is a white solid very soluble in water to give mildly acidic solutions. Ascorbic acid and its salts with sodium, potassium, and magnesium usually act as an antioxidant and are used in curing of different diseases like hypertension. Metal salts of ascorbic acid typically react with oxidants of the reactive oxygen species, such as the hydroxyl radical formed from hydrogen peroxide, and can terminate chain radical reactions.

2.2. Detection Measurement. Scanning electron microscope (Hitachi S-3000H) was used to observe the magnesium contents in the magnesite ore.

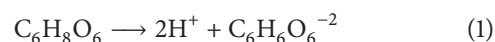
2.3. Experimental Procedure. Different size fractions (150–590 µm) were used in a 500 mL well-mixed spherical glass batch reactor, equipped with a mechanical stirrer, digital

controller unit, timer, and thermostat. Various experiments were carried out with known amount of ascorbic acid having different concentrations at various L/S ratios. Each time a known amount of the ascorbic acid was added slowly to the reaction vessel containing 5 g of magnesite ore. The vessel contents were stirred at a certain speed along with different times and temperatures. At the end of each experiment, an ice bath was used to stop the reaction in reaction vessel. The contents of reaction vessel were filtered using suitable filter paper. The filtrate solution was analyzed volumetrically for magnesium contents to evaluate the degree of conversion.

3. Mechanism of Leaching

The leaching process of the magnesite ore with ascorbic acid can be represented as follows.

(a) Ionization of $C_6H_8O_6$



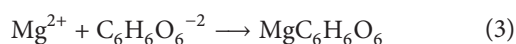
(b) Diffusion of H^+ ions to the exposed surface of the magnesite particles.

(c) H^+ ions attack on the magnesite particles in the rock:



The H^+ ions taking part in these reactions may come from the ascorbic acid as well as from the carbonic acid formed in the medium.

(d) Reaction between Mg^{2+} and $C_6H_6O_6^{-2}$



The leaching process can be represented by using the following general equation:



Solubility product constant for $MgCO_3$ is 7.46 at 25°C, and the ionization constants for ascorbic acid are $pK_1 = 4.10$, $pK_2 = 11.6$ at 25°C. Dissociation constants for carbonic acid are $pK_1 = 6.35$, $pK_2 = 10.33$ at 25°C. The equilibrium direction for the above reaction (4) remains in forward direction and may be considered as an irreversible reaction because one of the products (CO_2) produced during the reaction conditions is evacuated from the reaction mixture.

4. Results and Discussion

4.1. Morphology of Magnesite. The SEM micrograph of the raw magnesite ore has been shown in Figure 2, which indicates the morphology of magnesite ore. The material seems to be nongranular with surface roughness. The surface roughness is due to the evolution of volatiles which in this case might be CO_2 .

TABLE 1: Chemical analysis of natural magnesite ore.

Component	[Wt %]
MgO	45.4
CaO	1.18
Fe ₂ O ₃	0.8
SiO ₂	0.52
Loss on ignition [at 950°C]	52.1

TABLE 2: EDX analysis of natural magnesite ore.

Element	[Wt %]	[Atomic %]
C	14.90	20.79
O	56.907	59.50
Mg	27.24	19.02
Si	0.242	0.14
Ca	0.836	0.35
Fe	0.56	0.17

4.2. Effect of Reaction Temperature. The effect of temperature (40°C to 70°C) on rate of conversion of magnesite ore was investigated at different experimental conditions (178 micrometer particle size, 10% ascorbic acid with liquid/solid ratio of 10:1, and 350 rpm) as shown in Figure 3. It was observed that the rate of conversion of the magnesite ore increased with an increase in reaction temperature. It was also observed that increase in temperature reduced the reaction time required to attain the equilibrium in reaction medium. Furthermore, higher temperature (above 70°C) can cause contamination of CO₂ gas stream with ascorbic acid and water vapors. The experimental results indicated that the reaction temperature was the most effective parameter in the dissolution kinetics of magnesite ore. From these experimental observations it was also evaluated that below 40°C the ascorbic acid was not good leaching agent due to its lower solubility.

4.3. Effect of Acid Concentration and Liquid Solid Ratio. Different experiments were carried out to find the effect of concentration of ascorbic acid and liquid solid ratio on leaching kinetics of magnesite ore under various experimental reaction conditions as given in Figures 4 and 5. The experimental results indicated that an increase in acid concentration caused an increase in magnesium content. However, after certain optimum value of acid concentration, the increase in acid concentration did not have an appreciable effect. It might be considered that when the acid concentration exceeded its maximum required value, the hydrogen ions in the medium might decrease due to decrease in water contents. During the leaching study of colemanite ore with acetic acid, Özmetin et al. [24] found that higher acid concentration in reaction medium increased the rate of appearance of product by attaining the saturation value along with the formation of sparingly solid film layer resulting in a decrease in dissolution process.

From Figure 4, it was found that the acid concentration of 10% was good for leaching kinetics study of magnesite

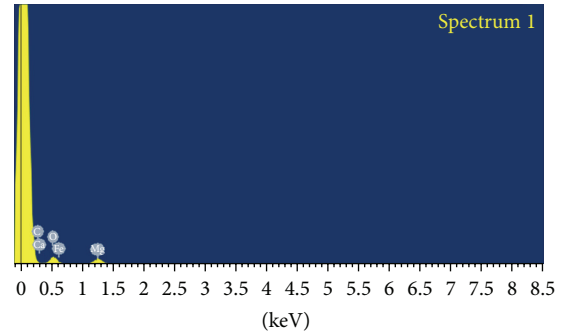


FIGURE 1: EDX pattern of natural magnesite ore.

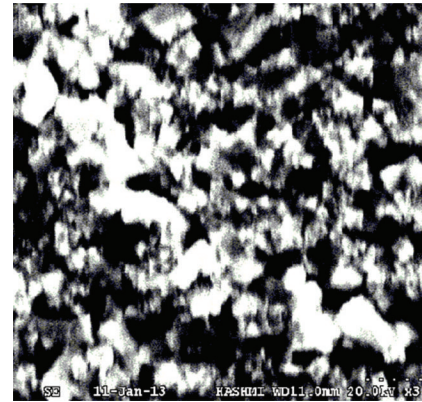


FIGURE 2: SEM image of natural magnesite ore.

ore with liquid solid ratio of 10:1. The pH of reaction medium depends on the ascorbic acid concentration and its degree of ionization at a particular temperature. The pH decreased as the concentration of ascorbic acid was increased. Figure 5 showed that the rate of dissolution of magnesite ore increased with an increase in the liquid solid ratio. From the experimental results, it was found that the liquid-solid ratio also had a significant effect on dissolution rate of magnesite ore. It may be attributed to the fact that a relatively higher liquid solid ratio may provide a medium of liquid phase to facilitate the mobility of reactive species produced in the reaction medium.

4.4. Effect of Particle Size. In order to investigate the effect of particle size on the leaching of magnesite ore different experiments were carried out. Four different size fractions of magnesite ore (150, 178, 297, and 590 μm) at 60°C were used to find the effect of particle size as shown in Figure 6. The leaching curves indicated that the rate of dissolution process increased as the particle size was decreased. This situation might be attributed to the fact that the surface area for reaction becomes more available with decreasing particle size resulting an increase in the efficiency of the leaching process. In separate experiments, it was observed that the effect of stirring speed on the leaching reaction rate was not appreciable as compared to the other parameters. This

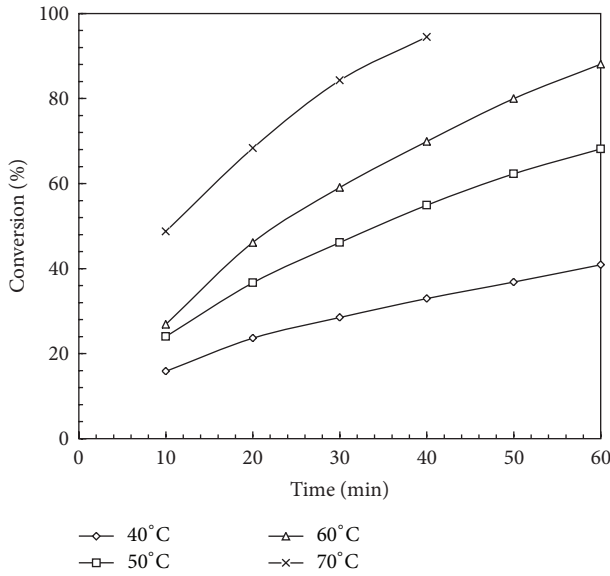


FIGURE 3: Effect of temperature on leaching of magnesite ore.

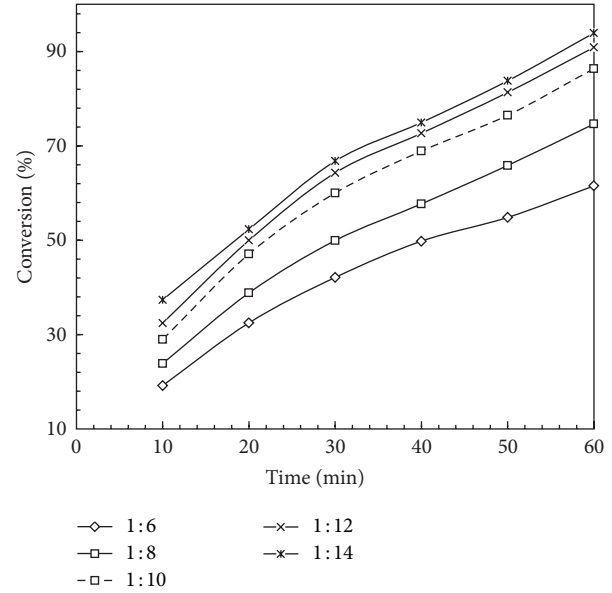


FIGURE 5: Effect of liquid solid ratio on leaching of magnesite ore.

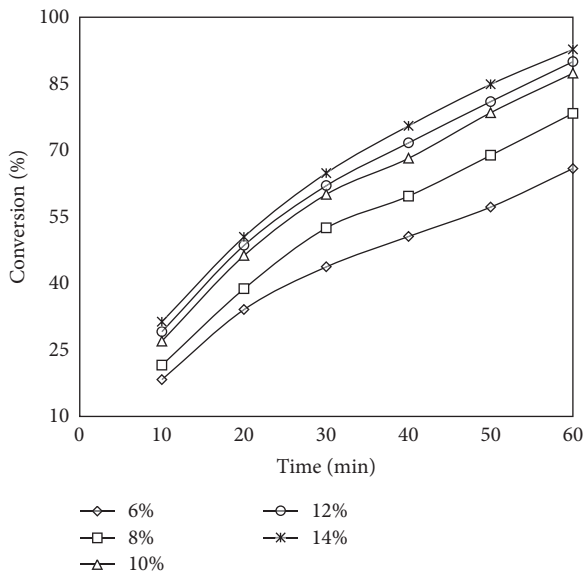


FIGURE 4: Effect of ascorbic acid concentration on leaching of magnesite ore.

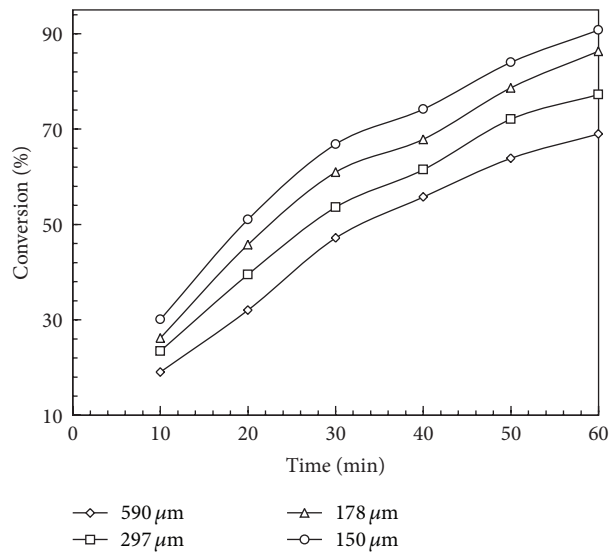


FIGURE 6: Effect of particle size on leaching of magnesite ore.

situation indicated that the leaching of magnesite ore was not product or ash layer controlled process.

5. Kinetic Analysis

Fluid solid heterogeneous reaction systems are usually involved in chemical and hydrometallurgical processes. In fluid solid reaction systems, reaction rate may be controlled by one of the following mechanisms: diffusion through the fluid films, diffusion through ash/product layer, or the chemical reaction at the surface of the core of unreacted materials [25]. The experimental data was analyzed on the basis of shrinking core model to find rate controlling step and

kinetic parameters. The reaction between a solid and fluid can be represented as



If no ash/product layer over unreacted core is formed, then two controlling steps may be fluid film diffusion or chemical reaction. If the time of completion of the leaching process is k_o , the fractional conversion of magnesite is x and at any time t the integrated equations for fluid-solid heterogeneous reactions may be represented as follows.

For film diffusion control,

$$t = k^* [1 - (1 - x)]. \quad (6)$$

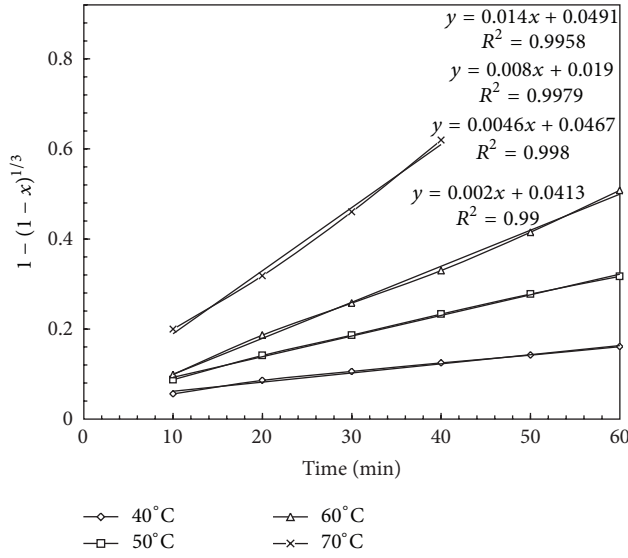
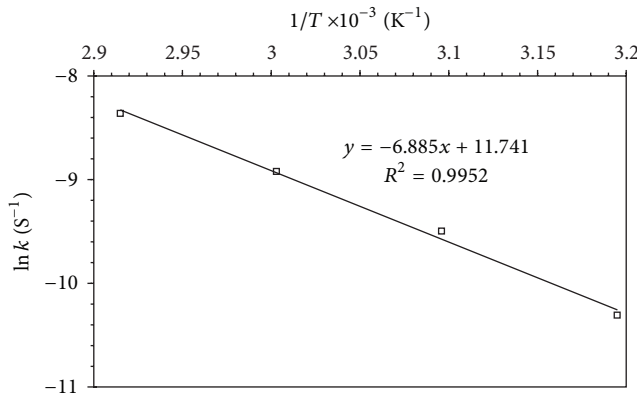
FIGURE 7: $1 - (1 - x)^{1/3}$ at different reaction temperatures.

FIGURE 8: Arrhenius plot for leaching of magnesite ore.

For chemical reaction control,

$$t = k^* [1 - (1 - x)^{1/3}]. \quad (7)$$

The value of k^* may vary with reaction parameters according to the kinetic models. For example, according to the chemical reaction controlled model (7), k^* is

$$k^* = \frac{\rho_B R_o}{b K_s C_A}, \quad (8)$$

where k^* is the time for complete dissolution (min), ρ_B is the molar density of the solid reactant (mol m^{-3}), R_o is the radius of the solid particle (m), b is the stoichiometric coefficient of the solid, K_s is the surface reaction rate constant (m min^{-1}), and C_A is the leaching agent concentration (mol dm^{-3}). The validity of the experimental data into the integral rate was tested by statistical and graphical methods. The kinetic analysis results for the dissolution process were found to be consistent with a chemically controlled reaction and the

integral rate expression was determined to obey the following rate equation:

$$1 - (1 - x)^{1/3} = kt. \quad (9)$$

Using the conversion values for various reaction temperatures, liquid solid ratio, stirring speed, particle size fractions, and acid concentration applied in leaching kinetics of magnesite ore, the apparent rate constants k can be evaluated by plotting $1 - (1 - x)^{1/3}$ versus t as shown in Figure 7. Using the Arrhenius equation, the above equation may be expressed as

$$1 - (1 - x)^{1/3} = k_o e^{-E_a/RT} t. \quad (10)$$

Arrhenius plot for the leaching of magnesite ore in ascorbic acid solutions was obtained by plotting the values of slopes of the straight lines (apparent rate constant) versus $\ln(1/T)$ as shown in Figure 8 and the following values were calculated:

$$1 - (1 - x)^{1/3} = 1.256 \times 10^5 e^{-57244/RT} t. \quad (11)$$

The value of activation energy indicates that the leaching of magnesite with ascorbic acid solutions is controlled by chemical reaction, and this value agrees with the values obtained in the similar research work of fluid solid reaction system [26]. Abdel-Aal [27] described that the activation energy of a diffusion controlled process is characterized to be from 4.18 to 12.55 kJ mol^{-1} , and, for a chemically controlled process, value of activation energy is usually greater than 41.84 kJ mol^{-1} .

6. Conclusions

- (i) The experimental results show that the ascorbic acid can be used as leaching agent to extract magnesium contents from the magnesite ore.
- (ii) Analysis of the kinetic data by different kinetic models shows that the leaching of magnesite ore in ascorbic acid solutions follows a chemically controlled process with activation energy of 57.244 kJ mol^{-1} .
- (iii) In the leaching of magnesite ore with ascorbic acid, the product, that is, magnesium ascorbate obtained is an important medical material and can be used in curing of different diseases like hypertension.
- (iv) Nontoxic techniques in terms of environmental pollution and human safety are the major reasons in using environment friendly leaching agents like ascorbic acid for the dissolution studies of magnesite ores.

Explanation of Symbols

- E_a : activation energy (J mol^{-1})
 x : dissolved fraction of Mg^{2+}
 L/S : liquid/solid ratio ($\text{cm}^3 \text{g}^{-1}$)
 t : reaction time (min)
 T : reaction temperature (K)
 k : reaction rate constant (min^{-1})
 EDX : energy dispersive X-ray analysis.

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