MAGNESITE ORE DISSOLUTION WITH ORGANIC ACID AND PARAMETRIC CUMULATIVE EFFECT OF REACTION PARAMETERS

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ABSTRACT: *Organic acids are considered relatively weak as compared to mineral acids. In the current study succinic acid has been used as a leaching agent to extract magnesium from magnesite ore. In order to evaluate the influence of various reaction parameters (temperature, liquid/solid proportion, strength of leaching agent and particle size of sample) on the dissolution and reaction kinetics of magnesite, a series of tests have been conducted. The outcomes of the leaching process show that the dissolution rate of magnesite is affected by temperature, acid solution concentration & liquid/solid ratio while it is inversely related to particle size. The multiple regression has been applied to analyze the experimental data. The results indicate that the extraction of magnesium from magnesite ore follows the following semi empirical reaction kinetic model i.e.;*

$$1-(1-\alpha)^{1/3}=0.376\ C^{1.31288}(L/S)^{1.2650}D^{-0.4355}S^{0.8106}e^{-43211/RT}t.$$

The calculated activation energy (43.2 kJ/mole) illustrates that the dissolution of magnesite with succinic acid is a chemically surface controlled reaction.

Key words: Succinic acid; Magnesite; Leaching kinetics; Regression analysis; Parametric cumulative effect; Kinetic model

1. Introduction

Magnesium is the third most ordinarily used structural metal after iron and aluminum. Magnesium and its compounds find diverse applications in Grignard reagent synthesis, medicinal products, alloys formation, textile, pyrotechnics and many other areas [1]. Magnesite is considered as one of the most suitable ores for procurement of magnesium and its various compounds. The impurities which are generally present in magnesite are calcium, iron, silica, etc. and these can be the basis of unwanted effects on the usage of compounds of magnesium.

The literature concerning the applications of different leaching agents for the dissolution studies of various rocks is available [2-5]. Various leaching agents have been applied for dissolution of magnesite rocks. Abali et al. [6] used inorganic acid (sulfuric acid) for the dissolution of magnesite and showed that the rate determining step is a chemically controlled. On account of certain limitations of inorganic acids (difficulty in achieving pH control of the reaction medium, poor selectivity and high rates of corrosion of the reaction vessels) organic acids can be considered as active leaching agents. Organic acids may be preferred for leaching of ores where comparatively less acidic strengths are applicable. Moreover, organic acids may be obtained from renewable biological sources.

Zafar and Ashraf [7] used lactic acid for dissolution of calcareous phosphate rocks and found that chemical reaction step is the rate determining step. The studies related to dissolution of magnesite in ascorbic acid, formic acid, citric acid, acetic acid, lactic acid as well as in gluconic acid are available [4, 8-12]. From the findings it was inferred that the leaching reaction was determined by surface chemical step. No studies have been found concerning the parametric cumulative effects on the kinetics of ore of magnesite with succinic acid solutions. Bashir et al. [13] has reported that the magnesite ore deposits are abundantly located in Khuzdar (Pakistan). The report illustrates that these deposits are of Kraubath type associated with alpine type bela ophiolite of cretaceous. No systematic studies have been reported for the parametric cumulative effect on the kinetics of indigenous magnesite deposits with succinic acid. Therefore, indigenous ore of magnesite has been undertaken to explore its leaching with succinic acid solutions and to investigate the parametric cumulative effect of different reaction parameters on its leaching kinetics. Moreover, succinic acid is commercially obtained from biological sources such as fermentation of glucose [14].

2. EXPERIMENTAL

2.1. Preparation of Samples and their analysis

The samples of magnesite were collected from Khuzdar (Pakistan). These samples were crumpled with ball mill and further ground by mortar grinder, sieved to obtain particle size fractions (150, 178 and 297 µm) using Tyler mesh screens. All the sieved samples were dried up at 100 °C in an electric oven. The dried samples were taken to ambient temperature and kept in dry glass vessels. In order to analyze the magnesite samples, instrumental techniques such as atomic absorption spectrometer (AAS) and X-ray diffractometer (XRD) were used along with the other conventional techniques such as standard gravimetric and volumetric methods [15]. All the chemicals used in this study were of reagent grade. The stock solutions and their further dilutions were made in deionized water.

2.2. Experimental procedure

Leaching and dissolution studies of magnesite samples were undertaken using different particle sizes (150, 178 and 297 µm) in a glass batch reactor having capacity of 500 ml, furnished with a mechanical stirrer for effective mixing, thermostat for temperature control, timer for controlling leaching time and a cooler for terminating the reaction. A number of trials were undertaken with specific volume of succinic acid at various liquid/solid proportions. In each experiment a defined volume of the leaching agent was inserted gradually to the glass vessel having 5 g of magnesite sample. After completion of each experiment, the glass reactor contents were filtered to remove insoluble impurities.

Table-1: Analysis of a naturally occurring magnesite sample.

Constituents	[Wt.%]
MgO	45.5
CaO	1.2
Fe_2O_3	0.4
SiO_2	1.7
Loss on ignition [at 950 ^oC]	51.2

The degree of conversion for magnesium contents was determined by analyzing filtrate solution volumetrically [15]. The impurities contained by magnesite ore such as calcium and iron may react with succinic acid and form their less soluble succinate salts [16, 17].

3. RESULTS AND DISCUSSION

An X-ray diffraction pattern (Fig. 1) of natural magnesite sample obtained from Bruker D8 shows the presence of major and minor phases. The results from the analysis of calcined indigenous magnesite using atomic absorption spectrometer, are given in Table 1, which depicts the presence of MgO as a main component of magnesite samples.
The influence of reaction temperature (45 $^{\circ}C$ to 75 $^{\circ}C$) on extraction of magnesium from magnesite samples was determined using various reaction parameters (178 µm sample particle size, 7 % (g/100 ml) succinic acid with liquid to solid proportion of 20:1 ml/g and a stirring speed of 350 rpm), was investigated. The rate curves in Fig. 2 show that the recovery of Mg from magnesite is amplified with rise in temperature and with a corresponding reduction in time of reaction.

Table-2: The regression results for the parametric cumulative effect on Arrhenius parameters

Model	$\ln k_o$	E_a/R	a	b	c	d	SE	R^2	observations
Eq. (11)	12.056	5444.75					0.0763	0.9824	25
Eq. (12)	8.9678	5326.33	1.3821				0.1078	0.9605	49
Eq. (13)	4.6418	5262.25	1.3477	1.2977			0.1442	0.9227	85
Eq. (14)	3.7726	5239.29	1.3355	1.2862	-0.4497		0.1361	0.9189	105
Eq. (15)	-0.9785	5197.20	1.3129	1.2650	-0.4355	0.8106	0.1378	0.9105	137

The influence of concentration of leaching agent (succinic acid) and liquid to solid fraction on rate of conversion of magnesite was found as shown in Fig. 3 & 4 respectively. From the Fig. 3, it can be seen that an escalation in concentration of succinic acid results in rise in rate of conversion of magnesite. However, succinic acid concentration higher than 7% has not any considerable impact on the dissolution of magnesite. Ozmetin et al. [18] investigated the dissolution of colemanite ore with acetic acid and found that higher leaching agent amount in reaction medium elated the rate of product formation with the appearance of sparingly solid film layer which results in fall in leaching reaction.
A number of experiments were done by varying the liquid to solid fraction from 15:1 to 22.5:1 ml/g to find the impact of liquid to solid ratio on the recovery of magnesium. The results are shown in Fig. 4, which shows that the dissolution of magnesite increases with rise in the liquid to solid ratio from. Liquid to solid ratio of 20:1 ml/g was considered as suitable for leaching of magnesite, since higher liquid solid ratios increase difficulty in handling and raises the time of evaporation to obtain product.

The effect of sample particle size and stirring speed on the leaching of magnesite is shown in Fig 5 & 6. The leaching reaction kinetics of magnesite ore was determined using four different size fractions (150, 178 and 297 µm) at 65 $^{\circ}C$ reaction temperature, 7 % succinic acid concentration, 20:1 ml/g liquid to solid ratio and 350 rpm rate of stirring. As expected the rate of reaction increases with the decrease in particle size of magnesite ore (Fig. 5). This situation is attributed to the fact that lessening in particle size causes rise in surface area for the reaction and results in an increase in dissolution rate. Further decrease in particle size of magnesite will elevate the intake of energy for grinding and will result in an increase in reaction cost.
In order to probe the influence of rate of stirring on dissolution of magnesite, stirring rates were varied from 250 rpm to 400 rpm. The results shown in Fig.6, indicate that the effect of rate of stirring on the dissolution process of magnesite ore is not much momentous. This situation may be due to the fact that the leaching of magnesite in succinic acid is not an ash layer or product controlled reaction.
The economy of a process is also governed by the cost of chemicals used. Succinic acid can be regenerated by treating

magnesium succinate (reaction product) with any mineral acid. In this way selectivity of succinic acid can be favorably used without experiencing the higher costs. Moreover, in order to obtain pure MgO the solid magnesium succinate can be evaporated and combusted in air as in similar studies of making PbO from lead citrate crystals [19]. It is also possible to use magnesium succinate as a value-added pharmaceutical product to treat magnesium deficiencies.

4. Kinetic analysis

The hydrometallurgical reactions frequently involve fluid-solid heterogeneous systems. According to Levenspiel [20], rate of reaction in fluid solid heterogeneous reaction systems is generally governed by one of the followings:

a) Fluid film control
b) Ash/product layer control
c) Surface chemical control (Topo-chemical control)

According to shrinking core model, a chemical reaction occurring between a fluid and solid may be denoted as:

$$X_{(fluid)} \quad + \quad yY_{(Solid)} \rightarrow \quad products \qquad (1)$$

In order to probe the reaction conditions and slowest step for leaching of magnesite, the analysis of the data was done by considering heterogeneous reaction models. The statistical and graphical methods were applied to find the validity of the data. The results for the leaching of magnesite were steady with a surface chemical rate expression as given below:

$$1-(1-\alpha)^{1/3} = kt \qquad (2)$$

The rate constants *k*, can be determined by plotting $1-(1-\alpha)^{1/3}$ *and*. t. Using the Arrhenius equation, the Eq. (2) can be denoted as:

$$1-(1-\alpha)^{1/3} = k_o\ e^{-E_a/RT}t \qquad (3)$$

The kinetic model (Eq. 3) can only explain the impact of reaction temperature on the dissolution phenomena of the ore. However, the specific values used for various reaction conditions (particle size of sample, stirring rate, liquid/solid proportion, and acid concentration) at different temperatures restrict its application. The designing of an industrial plant may not be able to give good results under the situations when the other reaction parameters like acid strength, particle size of sample, liquid to solid proportion and stirring rate also affect the rate constant along with the temperature. In such cases variation in experimentally determined values of activation energies may cause fluctuations in the dissolution processes.

Different semi empirical models are available for dissolution kinetics of different ores; however, a limited literature may be available to illustrate the cumulative parametric impact on Arrhenius variables for the dissolution of natural magnesite. In order to find the cumulative parametric impact on Arrhenius variables for the leaching of magnesite, the

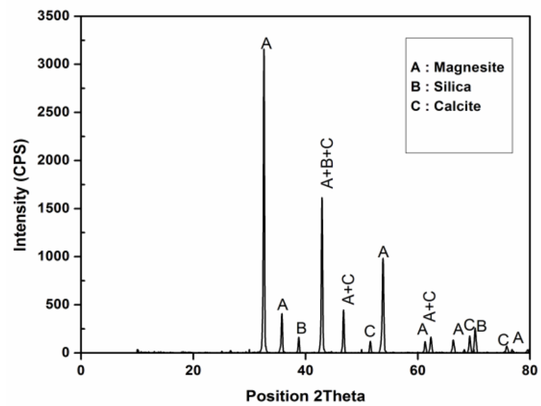

Fig. 1: XRD pattern of natural magnesite.

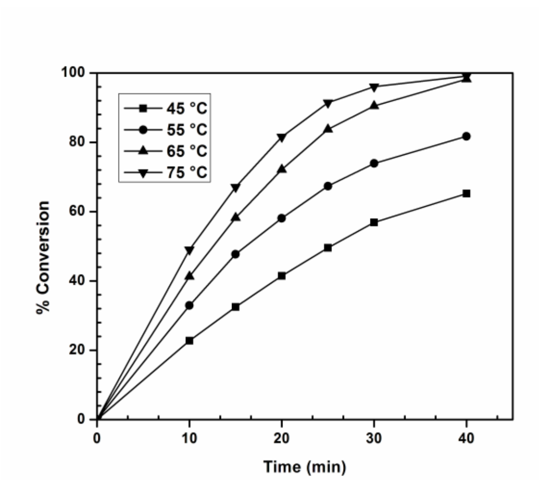

Fig. 2: Effect of reaction temperature on leaching of magnesite (7% succinic acid, 178 μm particle size, L/S ratio 20:1 ml/g, stirring speed 350 rpm).

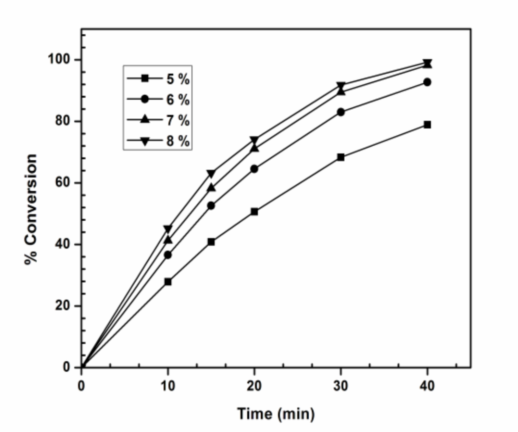

Fig. 3: Effect of concentration of leaching agent (178 μm, 20:1 ml/g, 65°C and 350 rpm).

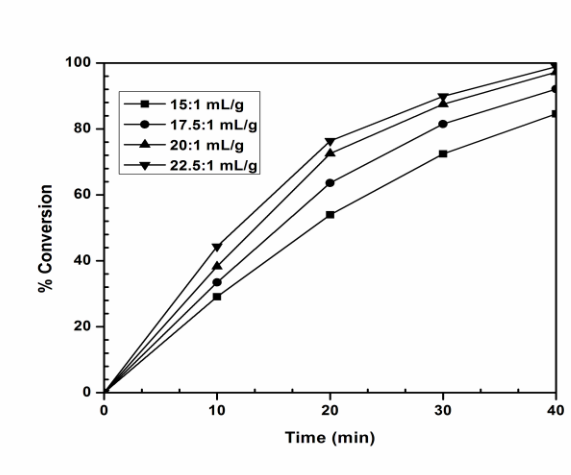

Fig. 4: Effect of liquid solid ratio on leaching of magnesite (7%, 178 µm, 65°C and 350 rpm).

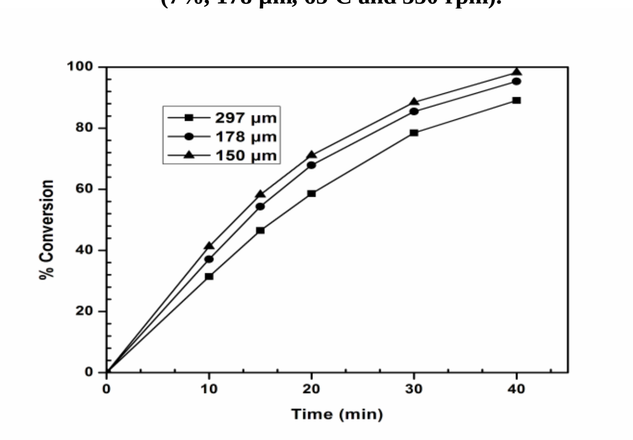

Fig. 5: Effect of particle size on leaching of magnesite (7%, 20:1 ml/g, 65°C and 350 rpm).

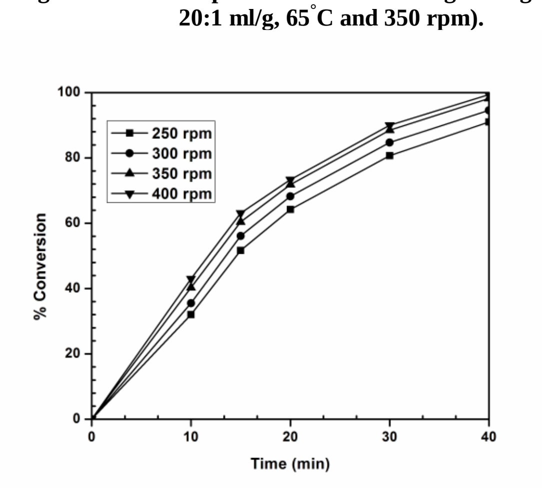

Fig. 6: Effect of stirring speed on leaching of magnesite (7%, 178 µm, 20:1 ml/g and 60°C).

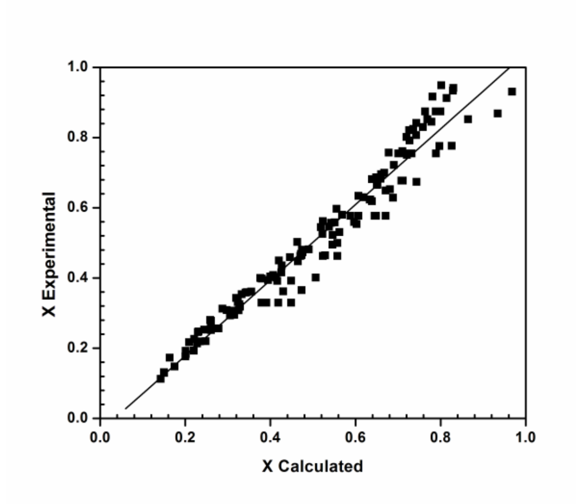

Fig. 7: Agreement between experimental and calculated conversion values of magnesite.

influence of different reaction conditions such as acidic strength, liquid/solid proportion, stirring rate and sample particle size on the kinetic models may be evaluated. Statistical multiple regression was applied to develop a semi empirical model. The reaction rate constant k involving parametric cumulative effect [21] can be expressed as:

$$k = k_o C^a e^{-E_a / RT} \quad (4$$

$$k = k_o C^a (L/S)^b e^{-E_a / RT} \quad (5)$$

$$k = k_o C^a (L/S)^b D^c e^{-E_a / RT} \quad (6)$$

$$k = k_o C^a (L/S)^b D^c S^d e^{-E_a / RT} \quad (7)$$

Where k is reaction rate constant, C the acid strength, D the sample particle size, L/S liquid/solid proportion, S stirring speed, E_a the activation energy, R, k_o, a, b, c, d, constants, T, the temperature and t reaction time. The values of the regression coefficients and constants shown in Table 2 were calculated using computer program for multiple regression. Using the values of the different parameters calculated from simultaneous regression analysis, Eqs. (3-7), can be written as,

$$1-(1-\alpha)^{1/3} = 1.7205\times10^5 e^{-45269/RT} t \quad (8)$$

$$k = 7.846\times10^3 C^{1.3821} e^{-44284/RT} \quad (9)$$

$$k = 1.037\times10^2 C^{1.3477} (L/S)^{1.2977} e^{-43751/RT} \quad (10)$$

$$k = 4.349\times10^1 C^{1.3355} (L/S)^{1.2862} D^{-0.4497} e^{-43561/RT} \quad (11)$$

$$k = 0.376 \quad C^{1.31288} (L/S)^{1.2650} D^{-0.4355} S^{0.8106} e^{-43211/RT} \quad (12)$$

The above equations (8-12) show that the insertion of reaction variables affect the Arrhenius parameters depending on different variable conditions used in the leaching process. From the comparison of equations (3) & (12), the following semi-empirical model may be developed:

$$1-(1-\alpha)^{1/3} = 0.376\ C^{1.31288}(L/S)^{1.2650}D^{-0.4355}S^{0.8106}e^{-43211/RT}t \quad (13)$$

From the simultaneous multiple regression analysis, the values of multiple correlation and determination of coefficient have been found to be 0.954 and 0.9104 respectively. These values indicate that the applicability of the above model is good. The results show that the most effective reaction parameter is temperature. In addition to the effect of temperature, comparison of equations (8) & (13) indicates that the concentration of acid, liquid to solid proportion, sample particle size and rate of stirring also affect the kinetics of the leaching of magnesite. The findings show that the impact of acidic concentration is relatively higher in contrast to the influence of liquid to solid proportion used in the leaching process. The activation energy value shows that the dissolution of natural magnesite with succinic acid is governed by surface chemically controlled step.

The correlation between experimental and theoretical conversion values was checked to evaluate their relationship. The correlation between experimental conversion and calculated values is shown in Fig. 7, which illustrates the tendency of the kinetic data to exist around the line of regression. From this scatter diagram, it is found that the relationship between X_{exp} and X_{cal} is good. The values of coefficient of determination (0.96) and standard error of estimates (0.137) were also calculated. Such values indicate the occurrence of a good agreement between the two variables and the scattering of the observed values around the line of regression is small. These values also show the close agreement between X_{exp} and X_{cal} for the leaching of the magnesite ore.

To test the workability of the suggested kinetic model, the relative mean square of errors was also determined. The relative mean square of errors (0.0093) for 137 experimental observations also fairly supports the applicability of the kinetic model. It may be concluded that in such probabilistic models, the values of these errors are not substantial and therefore, the workability of the proposed kinetic model is good.

5. CONCLUSION

- The results show that succinic acid can be used as a leaching agent to extract Mg contents from a magnesite ore.
- Cumulative Parametric effect on Arrhenius variables is determined to illustrate the combined effect of different parameters used in the leaching kinetics.
- Analysis of the kinetic data indicates a surface chemical reaction with energy of activation of 43.2 kJ mol^{-1}.
- The values of multiple correlation and determination of coefficient indicate that the workability of the suggested kinetic model is good.
- The results show that the most effective parameter is temperature, however, the concentration of the leaching agent, liquid to solid proportion, rate of stirring and sample particle size also affect the leaching reaction kinetics.
- The economy of the leaching reaction of magnesite mainly depends on the cost of succinic acid which may be regenerated by treating magnesium succinate with any inorganic acid thus taking advantage of selectivity without incurring cost penalties.

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