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Investigation of dissolution kinetics of natural magnesite in gluconic acid solutions

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Abstract

In this study, the dissolution of magnesite particles in aqueous gluconic acid solutions was investigated in a batch reactor employing the parameters of stirring speed, particle size, temperature, solid/liquid ratio and acid concentration. The shrinking core model was evaluated for the rate increased by decreasing particle size and increasing the temperature and initially, the dissolution in terms of acid concentration and then fell with the increasing concentration. No important effect of stirring speed was observed and the dissolution rate decreased as solid/liquid ratio increased. It was shown that the model is:

$$-2.0\ \ln((1-X_\mathrm{B})^{1/3}+1.63)+1.0\ \ln((1-X_\mathrm{B})^{2/3}-1.63(1-X_\mathrm{B})^{1/3}+2.66)-3.47\arctan(0.58(1.23(1-X_\mathrm{B})^{1/3}-1))=\frac{3bk_\mathrm{S}C_\mathrm{A0}}{\rho_\mathrm{B}R}t$$

Dissolution curves were evaluated in order to test shrinking core models for fluid–solid systems. Consequently, it was determined that the dissolution rate is controlled by surface chemical reaction. The activation energy of the process was determined to be 61.7 kJ mol^{-1}.

Keywords: Magnesite; Gluconic acid; Chemical dissolution; Kinetics

1. Introduction

Dissolution of the solid particles is a typical industrially relevant process, for instance in hydrometallurgy, medicine, oceanography, crystallography, ceramics and desalination as well as in a number of biological and environmental precipitation processes [1]. One of the solid particles is magnesite ore. Turkey has extensive magnesite ores. Magnesite (magnesium carbonate) is found in three main forms: (1) crude magnesite, primarily for use in chemicals, pharmaceutical industry as an anti-acid, agriculture, lime, in paper and sugar industries, (2) dead-burned magnesia, a durable refractory for use in cement, pharmaceutical industry, glass, steel and which is used in the metallurgical industries and (3) caustic calcined magnesia, for use in making oxychloride and oxysulfate cements and various environmental and chemical applications.

Several studies have been performed to determine the dissolution rate of magnesite. They found that the layer of the product film formed on the mineral surface affects the reaction rate and the level of this effect differs for every acid [2]. Raschman and Fedorockova [3] were researched the kinetics of the reaction between dead-burned magnesite and hydrochloric acid. They found that the dissolution of MgO is controlled by the chemical reaction of MgO with H^+ and apparent activation energy was 58–64 kJ mol^{-1} [3]. Dissolution kinetics of magnesite mineral in water with chlorine was investigated depend on temperature, solid/liquid ratio, stirring speed, particle size and gas flow rate [4]. Another chlorination study of magnesite was realized by Kennedy and Harris and the activation energy for this process was calculated as 80 kJ mol^{-1} [5]. Also, a kinetic study of the dissolution of magnesite in HCl and the kinetic analysis proved that the dissolution rate is controlled by the surface reaction [6]. Demir et al. were studied the leaching kinetics of magnesite in citric acid solutions and activation energy was obtained 61.35 kJ mol^{-1}. It was found that the dissolution rate was controlled by chemical reaction [7]. Similarly, the dissolution of magnesite in acetic acid being an organic acid was investigated by Laçin et al. Activation energy of leaching process was found

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Nomenclature

b	stoichiometric coefficient of solid B
C_A	concentration of acid reactant (mol L^{-1})
C_{A_0}	initial concentration of acid reactant (mol L^{-1})
E_A	activation energy (kJ mol^{-1})
k	reaction rate constant (s^{-1})
k_S	rate constant for surface reaction (m s^{-1})
k_0	frequency or pre-exponential factor (s^{-1})
N_A	moles of acid reactant
N_B	moles of solid reactant
N_{B_0}	initial moles of solid reactant
r_C	radius of unreacted core (m)
R	initial particle radius (m)
R_g	universal gas constant (J mol^{-1} K^{-1})
S	surface (m^2)
t	time (s)
T	temperature (K or °C)
V	reaction volume (L^{-1})
X_B	fraction of B converted, the conversion
X_{Mg}	fraction of Mg converted

Greek letter

ρ_B	molar density of solid reactant (mol L^{-1})

78.40 kJ mol^{-1}. It was determined that the reaction fits the chemical reaction controlled [8]. In the another study, the dissolution kinetics of calcite were researched in acetic acid solutions by Fred and Fogler and they found that dissolution is influenced by the transport of both reactants and products below pH 2.9 and pH values >3.7, the dissolution is controlled by the kinetics of surface reaction [9]. No study was found concerning the dissolution kinetics of magnesite in gluconic acid solutions.

Gluconic acid and gluconates having a great importance in manufacturing industries that are used in pharmaceutical, food, feed, detergent, textile, leather, photographic and concrete industries [10–12]. Gluconic acid and its salts can be produced by chemical, electrochemical, biochemical, bioelectrochemical methods [13–15]. Recently, one of the major method for producing gluconic acid and gluconates is fermentation [16]. Magnesium, calcium, sodium, zinc and manganese gluconate production by fermentation have been studied, by some researchers [17,18].

The dissolution kinetics of a solid compound depends on the processes taking place at the solid–liquid boundary; the processes are complex and involve both chemical reactions and mass transfer. The solid–liquid reactions can occur at the surface of the solid, in the film around the solid or in the liquid bulk phase. Different steps, such as mass transfer, chemical reaction and charge transfer, can determine the dissolution rate. The classical models used for solid–fluid reactions are the shrinking particle and shrinking core models. The shrinking core model has been suggested by many authors to be valid for leaching of magnesite [1].

Therefore, in this study, the dissolution kinetics of magnesite in aqueous gluconic acid solution was examined according to the modified shrinking core models, and the best fitted equation to the experimental data was determined. The effects of the particle size, acid concentration, reaction temperature, solid/liquid ratio and stirrer speed on the dissolution rate have been evaluated.

2. Materials and methods

The sample of magnesite ore used in experimental runs comes from a region of Refahiye, Erzincan, Turkey. A sample was completely soluble in HCl, its chemical composition was analyzed by the standard gravimetric and volumetric methods [19] and the chemical analysis results of the ore are given in Table 1. An X-ray diffraction pattern of the magnesite ore was obtained using a Rigaku 2000 JCPDS DMAX (29-1490) diffractometer (XRD) with Cu Kα radiation (30 kV and 30 mA and automatic monochromator) at a scanning rate 2θ of 2° min^{-1} (Fig. 1). In this figure, the XRD studies of the ore indicate $MgCO_3$ as the major compounds and $CaCO_3$, Fe_2O_3, SiO_2 as minor compounds.

After crushing and washing, the ore was ground and then sieved to different size fractions 1425, 725, 512, 338, 215, and 153 μm using ASTM standard sieves.

Gluconic acid used for leaching in these experiments was reagent grade (50 wt.% solution in water) Acros organics.

The dissolution process was carried out in a 500 mL cylinder glass batch reactor heated by a thermostat for keeping reactor contents at a constant temperature, equipped with a digital controlled mechanical stirrer, thermometer and a condenser to prevent losses by evaporation (Fig. 2). For each experiment, 250 mL volume of gluconic acid at a definite concentration was transferred into the reactor at the required temperature. The reaction was initiated by the addition of a small amount of magnesite, at time $t = 0$, while stirring the contents of the reactor at a certain speed.

From leaching solution, 2 mL sample were collected at the pre-determined time intervals and it was filtered immediately and the amount of magnesium in the leach solution was analyzed complexometrically by EDTA at the medium of buffer solution (about pH 10) [20]. For each experimental condition, the experiment was repeated twice, and the arithmetic average of the result of the two experiments was used in the kinetic analysis. The dissolution tests were performed as a function of several parameters, their range and values are given in Table 2.

Table 1
Chemical analysis of the magnesite

Component	Wt.%
MgO	47.3
CaO	0.43
Fe_2O_3	0.25
SiO_2	0.40
Loss on ignitation (at 850 °C)	51.62