



Utilization of formic acid solutions in leaching reaction kinetics of natural magnesite ores



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ARTICLE INFO

Article history:

Received 12 November 2013
Received in revised form 22 June 2014
Accepted 16 August 2014
Available online 24 August 2014

Keywords:

Magnesite
Formic acid
Dissolution kinetics
Regression analysis
Kinetic model

ABSTRACT

In the present research work, dissolution kinetics of natural magnesite is carried out using formic acid as a leaching agent. The effect of various reaction parameters such as temperature, acidic solution concentration, particle size and liquid to solid ratio was studied regarding the leaching kinetics of natural magnesite. The findings show that the dissolution process is controlled by the chemical reaction (intrinsic) at the liquid-solid interface;

$$1 - (1 - x)^{1/3} = 59.41 \times 10^1 e^{-42078/RT} t.$$

The apparent activation energy of the leaching process of magnesite with the formic acid was found to be 42.08 kJ mol⁻¹ over the reaction temperature range of 318 to 348 K.

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1. Introduction

Magnesium, the 6th most common element, does not occur freely in nature because of its high reactivity. It is abundant in magnesite, periclase, asbestos, meerschaum, serpentine, talc and epsomite (Deangelis et al., 2007). Magnesium is important in many aspects of life and its uses involve synthesis of Grignard reagent, alloy formation, sulfur removal in iron and steel production, refractory materials, fertilizers, medicinal products, and fireproofing (Bukovisky, 1997; Jones et al., 2000).

A wide range of studies have been reported on leaching and dissolution kinetics of rocks with a variety of leaching agents (Demirkiran, 2008, 2009; Demirkıran and Künkül, 2007; Demirkiran and Kunkul, 2008; Dogan and Yartasi, 2009; Kovacheva et al., 2001; Kuslu and Colak, 2010; Mergene and Demirhan, 2009; Sandstrom and Samuelsson, 2010; Zhang and Nichol, 2010). In these research studies, it has been described that the leaching kinetics of different metal ores may vary with the change in nature and type of rock deposits. Leaching of magnesite rocks can be achieved by acids (inorganic/organic) or bases and their salts (Lacin et al., 2005). The studies on the dissolution process of magnesite in inorganic acids such as HCl, H₂SO₄ (Abali et al., 2006; Chou et al., 1989) showed that the controlling mechanism for the dissolution of magnesite is a chemical process. Inorganic acids have issues of selectivity, froth formation and scaling (Housmanns et al.,

1996). Conversely, organic acids can act as active leaching reagents because most of the leaching reactions are done in mild acidic conditions (pH 3–5). Moreover, organic acids have a low risk of corrosion and can be utilized for carbonaceous rocks. Another advantage of organic acids as leaching agents is their biodegradability, which generally depends on the carbon chain and other attached groups.

From leaching investigations of naturally occurring magnesite materials in acetic acid, gluconic acid, citric acid and lactic acid solutions, it was found that leaching kinetics were driven by chemically controlled mechanisms (Bayrak et al., 2010; Lacin and Bakan, 2006; Lacin et al., 2005).

Magnesite ore deposits are found abundantly in the Khuzdar areas of Balochistan (Pakistan). The Khuzdar area consists of a number of Kraubath type magnesite deposits associated with alpine type bela ophiolite dating from the cretaceous period (Bashir et al., 2009). These are mostly serpentized and harzburgite confined mostly in the lowermost segment of bela ophiolite. These deposits have not been considered extensively for leaching kinetic investigations up to this time. Moreover, no literature has been reported concerning formic acid as a leaching agent for the study of leaching kinetics of indigenous magnesite.

Therefore, the current research work was intended to investigate the leaching reaction kinetics of the indigenous magnesite ore by formic acid. The product formed (magnesium formate) can be used in animal feed formulations and in general chemical applications (Shi et al., 2005). It can also be used for determining pesticides in fruits and vegetables and for the simultaneous determination of tropane alkaloids and glycol alkaloids in grains and seeds.

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2. Experimental procedures

2.1. Sample protocol and analyses

Samples of magnesite involved in the current study were collected from the Khuzdar area in the province of Balochistan (Pakistan). Samples were ground in a ball mill followed by a mortar grinder. Different size fractions (500–707, 250–354, 177–210 and 125–177 μm) were obtained from screening of ground samples by ASTM sieves, and then dried in an electric oven at 100 °C for 24 h. These samples were brought to room temperature and stored. Atomic absorption spectrometry, scanning electron microscopy and other conventional methods (Furmann, 1963) were applied for the analysis of magnesite rock fractions. The formic acid (methanoic acid), EDTA (ethylene diamine tetra acetic acid) and EBT (eriochrome black T) used during analysis were of reagent grade. The preparation of stock solutions and their further dilutions were made using deionized water. Eriochrome black T and EDTA were used in volumetric quantitative determinations of magnesium in leached solutions. In complexometric titrations of magnesium (Gulensoy, 1974), EBT acts as an indicator while EDTA is used as a complexing agent for Mg.

2.2. Detection measurements and analytical procedure

Atomic absorption spectrophotometer (Hitachi-1800) was used for the determination of Mg in natural magnesite samples. Scanning electron microscope (JEOL JED-2300) was used to observe the particle morphology of raw magnesite. Leaching studies of magnesite samples were investigated in a reactor made up of glass with 500 mL capacity. A hot plate (IKA C-MAGHS-7) equipped with a temperature sensor (ETS-D5) was used to stir, heat and control the temperature (± 0.5 K) of the reactor contents. In each experiment, a fixed volume of 8% formic acid having an L/S ratio of 14:1 mL/g was gradually introduced to the reactor with 5 g of sample. These entities were agitated with stirring rate of 350 rpm at known times and temperatures. After completion of the reaction, the hot solution was filtered to remove gangue minerals from magnesium formate. The filtrate solution was analyzed to find the percentage of conversion of magnesite (Gulensoy, 1974).

3. Results and discussion

3.1. Sample characterization

To find loss on ignition, magnesite rock samples were heated to 950 °C for 24 h in a furnace. The carbonates of different elements were converted into their oxides with the liberation of CO_2 . The chemical composition of the calcined magnesite sample (Table 1) was determined by atomic absorption spectrometer. Table 1 indicates that magnesium is present in relatively higher concentrations than the other elements. The EDX spectrum of the intact ore of magnesite (Fig. 1) depicts the elemental composition. The elemental composition showing the mass and atomic % of different elements in the indigenous magnesite is given in Table 2. From the EDX signature, it can be inferred

that the material under study is magnesium rich. The profile also exhibits the presence of carbon and oxygen indicating the presence of carbonates. The magnesite in pure form is usually white in appearance but becomes colored due to the inclusion of impurities. The SEM image of the raw magnesite ore representing the apparent morphological properties of the magnesite is given in Fig. 2. The material appears to be non-granular with surface roughness, which may be due to the evolution of volatiles during the weathering and formulation of the ore.

3.2. Chemical reactions taking place in the glass reactor

Chemical reactions occurring in the reaction vessel containing magnesite and formic acid solution is represented as: (a) Formic acid ionization



(b) Diffusion of H^+ ions (c) Attack of H^+ ions on the magnesite particles



(d) Reaction between Mg^{2+} and formate ions



The ionization constant of formic acid is $\text{p}K_a = 3.75$ at 20 °C and the solubility product constant for MgCO_3 is 6.8×10^{-6} at 25 °C (Harned and Embree, 1934; Visscher et al., 2012). Ashraf et al. (2005) described that the magnitudes of the constants (ionization constant and solubility product constant) are generally temperature dependent and efficiency of the leaching reaction is restricted by the kinetics.

3.3. Effect of time and reaction temperature

The reaction temperature was varied from 45 °C to 75 °C to elucidate the influence of temperature on the rate of dissolution of magnesite while keeping the other experimental conditions constant (177–210 μm particle size, 8% formic acid, liquid/solid ratio of 14:1 mL/g and stirring speed of 350 rpm). The results are shown in Fig. 3, which illustrates that an increase in reaction temperature causes a rise in the rate of conversion of the magnesite. The elevation of reaction temperature from 55 °C to 75 °C in 30 min causes an increase in % recovery of magnesite from 49.8% to 84.9%. This situation indicates that an increase in the reaction temperature increases the rate of chemical reaction. Typical rate curves in Fig. 3 represent the temperature increase, which reduces the reaction time needed to achieve the maximum conversion. About 95% dissolution of magnesite is achieved at 75 °C in 40 min of leaching time. A number of experiments were carried out to determine the effect of formic acid concentration, L/S ratio in the medium and the particle size of magnesite on the dissolution kinetics of magnesite at 65 °C.

3.4. Influence of acid concentration and L/S ratio

In order to find the influence of concentration of formic acid on the leaching of magnesite, the concentration of formic acid was varied from 2% to 10% at a temperature of 65 °C, stirring rate 350 rpm and particle size fraction 177–210 μm . The results are shown in Fig. 4, which shows that an increase in acid concentration accelerates the rate of leaching of magnesite. However, concentrations higher than 8% do not have an appreciable effect as expressed in Fig. 4. This situation may be attributed to the fact that a relatively higher concentration of the leaching agent may attack the gangue minerals present in the ore. Ozmetin et al. (1996) described that an increase in the concentration of leaching agent in the reaction vessel may increase the product layer formation and produce a solid film layer surrounding the particles and

Table 1
Chemical composition of natural magnesite ore^a.

Component	(Mass.%)
MgO	43.47
CaO	0.38
Fe ₂ O ₃	1.11
SiO ₂	1.54
Loss on ignition (at 950 °C for 24 h)	53.5

^a Results obtained from analysis of magnesite ore by AAS (Hitachi-1800).

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