Journal of Industrial and Engineering Chemistry 18 (2012) 1202–1207

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Review

Leaching kinetics of colemanite in ammonium hydrogen sulphate solutions

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ARTICLE INFO

Article history:
Received 3 August 2011
Accepted 25 January 2012
Available online 2 February 2012

Keywords:
Colemanite
Ammonium hydrogen sulphate
Leaching kinetics

ABSTRACT

The aim of the study was to investigate the dissolution kinetics of colemanite in ammonium hydrogen sulphate solutions in a mechanical agitation system and to declare an alternative reactant to produce boric acid. Reaction temperature, concentration of ammonium hydrogen sulphate, stirring speed, solid/liquid ratio and particle size were selected as parameters on the dissolution rate of colemanite. The experimental results were successfully correlated by linear regression using Statistica Package Program. Dissolution curves were evaluated in order to test shrinking core models for solid–fluid systems. It was observed that increase in the reaction temperature and decrease in the solid/liquid ratio causes an increase the dissolution rate of colemanite. The dissolution extent is highly increased with increase the stirring speed rate between 100 and 500 rpm and the dissolution extent is slowly increased with increase the stirring speed between 500 and 700 rpm in experimental conditions. The activation energy was found to be 32.66 kJ/mol. The leaching of colemanite was controlled by diffusion through the ash or product layer. The rate expression associated with the dissolution rate of colemanite depending on the parameters chosen may be summarized as follows: $1-3(1-X)^{2/3}+2(1-X)=8.99\times C^{1.08}\times W^{1.39}\times D^{-1.27}\times (S/L)^{-0.54}\times e^{(-32.66/RT)}t$.

Contents

1. Introduction

Boron is widely distributed element in nature. It usually appears in the form of borat salts or boric acid. It is one of the most important underground richnesses of Turkey. Turkey has 72% of total world boron reserves on the basis of B_2O_3. It has more industrial and strategic importance. It occurs in traces in most soils and plants, but is only found in a concentrated form in a few places [1].

Boron compounds have found more increasingly field of application. It have gain more strategic importance and are used in hundreds of different fields as space technology, agriculture, nuclear industry or cleaning products. In recent years the production of boron and its compounds has increased greatly, as it can be used in nuclear engineering, as fuel for rocket motors, in

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1226-086X/$ – see front matter
doi:10.1016/j.jiec.2012.01.044

Nomenclature

b	stoichiometric coefficient
C	concentration of borax decahydrate solution (mol m^{-3})
C_{Ag}	concentration of A in the bulk solution (mol m^{-3})
D	mean particle size (m)
D_e	diffusion coefficient (m^2 min^{-1})
E_A	activation energy (kJ kmol^{-1})
k_d	mass transfer coefficient (m min^{-1})
k_s	reaction rate constant for surface reaction (mol min^{-1})
k_o	frequency or pre-exponential factor (min^{-1})
L	amount of liquid (mL)
n	mol number (mol)
r	correlation coefficient (–)
R	universal gas constant (kJ kmol^{-1})
R	initial radius of a solid particle (m)
S	amount of solid (g)
T	reaction temperature (K)
t	reaction time (min)
t^*	reaction time for complete conversion (min)
X	fractional conversion of B_2O_3
W	stirring speed (rpm)
ρ_B	molar density of solid reactant (mol cm^{-3})

hard and refractory alloys, in high quality steels, in the production of heat resistant polymers, for the production of optic and chemically stable glass in the glass industry. The compounds are also used in cosmetic, leather, ceramics, rubber, paint, textile and agricultural area and also as catalysts [2]. They also find application in the wood-processing industry as a protection against moulds. Borat and boric acid are used as raw materials for the manufacture of glass, soap, detergent, cosmetics and photographic chemicals, flame retardants and for nuclear installations as neutron absorbers.

Colemanite has a monoclinic crystal structure and a density of 2.40 g cm^{-3}. Its chemical formula is $2CaO \cdot 3B_2O_3 \cdot 5H_2O$. It is used to produce boric acid. Boric acid is used as a source of B_2O_3 in many fused products and as starting material in the preparation of many boron chemicals such as boron phosphate, boron tri halides, boron esters, boron carbide, organic boron salts and fluoroborates [3,4].

It has been known that the investigation of the dissolution of colemanite ore in various solutions have been studied for production of boron compounds. There are many studies in the literature connected with the dissolution kinetics of colemanite in various solutions.

Leaching kinetics of colemanite with different solutions has been studied by a number of investigators. These studies are summarized as follows: Alkan et al., studied colemanite ore in water saturated with CO_2. The process was found by chemically reaction controlled and the activation energy was calculated 57.7 kJ/mol [5]. Kocakerim and Alkan investigated it in water saturated with SO_2. The process was found by chemically reaction controlled and the activation energy was calculated 53.97 kJ/mol [6]. Karagölge et al. carried out it in ethylene diamine tetraacetic acid (EDTA). They found that the process was found by chemically reaction controlled and the activation energy was calculated as 50.60 kJ/mol [7]. The dissolution kinetics of colemanite was investigated in ammonium chloride by Kum et al., and they found that the dissolution was controlled by chemically reaction. The activation energy was found as 89 kJ/mol [8]. Özmetin et al. studied it in acetic acid. They carried out the process rate controlling step is the first order pseudo homogeneous reaction model. The activation energy was found as 51.49 kJ/mol [9]. The dissolution kinetics of colemanite was investigated in boric acid by Yartasi et al., and they found that the rate controlling step is diffusion through product film around unreacted core of colemanite particles [10]. Temur et al. investigated the dissolution kinetics of colemanite in phosphoric acid and they found the rate controlling step is surface chemically reaction process. The activation energy was calculated by 53.91 kJ/mol [11]. The dissolution of colemanite was carried out in sulphuric acid by Çetin et al. The process rate controlling step was found second order with respect to saturation level and the activation energy was found as 34.0 kJ/mol [12]. Alkan and Doğan were carried out experiments in oxalic acid and described the rate controlling step as product layer diffusion process. They found the activation energy as 39.70 kJ/mol [13]. Çavuş and Kuşlu studied the dissolution of colemanite in citric acid solution and the activation energy was found as 28.65 kJ/mol. The rate controlling step was diffusion thorough the product layer [14]. Tunç et al. investigated it in ammonium sulphate solutions. The rate controlling step is chemically reaction and the activation energy was found as 40.46 kJ/mol [15]. The dissolution kinetics of colemanite in perchloric acid was carried out by Gür and Alkan. Chemical reaction was found as rate controlling step and the activation energy was found as 46.47 kJ/mol [16]. Kubilay et al. was studied it in perchloric acid. Rate controlling step was heterogeneous chemical reaction and the activation energy was found as 41.07 kJ/mol [16]. Gür studied the dissolution kinetics of colemanite in amonioum nitrate solutions. The rate controlling step was chemically control and the activation energy was found as 41.40 kJ/mol [17]. Kuslu et al. was investigated it in potassium hydrogen sulphate solutions. Rate controlling step was diffusion through the ash or product layer and the activation energy was found as 26.34 kJ/mol [19].

The boric acid is industrially produced with a reaction between colemanite and sulphuric acid solution. As sulphuric acid is a strongly acid, the impurities in boron ore are dissolved. This case causes impurities in boric acid solutions. The quality of boric acid is reduced. Therefore, weak acid solutions should be used for production of boric acid.

The aim of our study is to investigate the dissolution kinetics of colemanite in ammonium hydrogen sulphate solutions in a mechanical agitation system and also to declare an alternative reactant to produce the boric acid. There is no study reported in the literature about such a procedure. Investigation on the dissolution conditions and the dissolution kinetics of colemanite in ammonium hydrogen sulphate will be beneficial to the solution of some problems appeared during boric acid production. So that, the kinetic data for the reaction of colemanite with ammonium hydrogen sulphate are very important for industrial application.

The dissolution kinetics of colemanite in ammonium hydrogen sulphate was examined according to the heterogeneous reaction models. In our study, reaction temperature, concentration of ammonium hydrogen sulphate, stirring speed, solid/liquid ratio and particle size were chosen as process parameters.

2. Methods and materials

Leaching experiments were conducted under atmospheric pressure conditions. All reagents used in the experiments were prepared from analytical grade chemicals (Merck) and distilled water. A constant temperature water circulator was used in combination with the reactor to maintain the mixture in the reactor at a constant temperature. The experiments were carried out in a 500 mL spherical glass reactor. The reactor was equipped with a reflux condenser to prevent evaporation during heating and