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ScienceDirect
Trans. Nonferrous Met. Soc. China 23(2013) 1797−1803
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Dissolution of thermally dehydrated ulexite in ammonium acetate solutions

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Received 27 July 2012; accepted 13 November 2012

Abstract: Ulexite, a boron mineral, contains a substantial amount of hydration water. Using calcination method, some part of water in the composition of solid can be removed from the solid matrix, and a porous structure can be obtained to increase the reaction rate. The dissolution of the calcined ulexite samples at various temperatures was investigated. Ammonium acetate was used as a leach reagent. The effects of some reaction parameters on the dissolution of the calcined ulexite were examined. It is found that the dissolution rate of calcined samples is higher than that of the uncalcined sample. The dissolution rate of the calcined ulexite is enhanced with increasing calcination temperature up to 150 °C. It is determined that the reaction rate conforms to the chemical reaction model. The activation energy of the dissolution process was calculated to be 41.5 kJ/mol.

Key words: calcination; dissolution kinetics; ulexite; boron mineral

1 Introduction

The borates are an unusually large group of minerals, but the number of commercially important borates is limited [1]. Most of the world's commercially recoverable reserves of boron are in the form of the hydrated metal borate minerals, such as pandermite, ulexite, tincal, and colemanite [2]. Boron is never found at free form in nature, and it is usually obtained in the form of boric acid and other compounds by acid leaching of boron-containing ores.

Boric acid and some other boron salts have an extensive industrial use in the production of glass, porcelain, leather, cosmetics and photographic chemicals, detergent materials, polymer, catalysts, steel and refractory materials, etc. Boron compounds are used in certain fertilizers for the treatment of boron-deficient soils. Boric acid, which has mild bactericidal and fungicidal properties, is also used as a disinfectant and food preservative [3,4]. Boric acid is also used as the starting material in the preparation of many boron chemicals, including synthetic organic borate salts, boron phosphate, fluoroborates, boron tri-halides and borate esters [5,6]. Boron minerals, such as colemanite and ulexite, are used as raw materials in the production of boric acid.

Boric acid can be produced by the solid-fluid reaction of the borate minerals with a leach reagent. The production of boric acid is performed from a reaction involving colemanite and sulfuric acid, in Turkey. In this production process, the ground colemanite reacts with an excess amount of sulfuric acid at 85−90 °C. Gypsum is formed as a by-product and precipitates in the reactor, while boric acid, which is highly soluble in water, remains in the liquid phase throughout the reaction. Gypsum is removed by filtration, and boric acid is crystallized by cooling the filtrate to about 40 °C [7−9]. Ulexite, a sodium-calcium-borate hydrate, has a chemical formula of $Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$, which is found in huge quantities in Turkey, and is commercially an important boron mineral. Ulexite is generally available together with other borates, and it can be used in addition to colemanite in the production of boron compounds due to the rapidly growing demand for various boron products [3,10]. In order to produce boric acid from ulexite, many studies have been performed using different leach reagents by various researchers [11−20].

Most of boron minerals include crystallization water in their structures. When minerals containing the water of crystallization, like ulexite, are subjected a heat treatment, they lose some part of hydrate water depending upon applied temperature. This process is known as calcination or dehydration. One of the goals of dehydration process is to obtain a porous solid for

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DOI: 10.1016/S1003-6326(13)62663-1

increasing the reaction rate in a solid-fluid reaction. The resulting porous structure allows more readily the occurring of the reaction between solid and fluid, and so the dissolution rate increases [21−23]. But, the dehydration process on the leaching rate of ulexite becomes effective till a certain dehydration temperature. During the dehydration process, some changes in the crystal structure of ulexite occur depending upon applied temperature. The porosity of ulexite increases with increasing the dehydration temperature. This provides an increment at the leaching rate. After a certain temperature, the sintering fact is observed with further heating the mineral. The sintering causes a decrease in the porosity of particle. Hence, the dissolution rate of ulexite decreases as a result of sintering [13,17,22,24].

Dehydration or calcination of ulexite was investigated [25−34]. The dissolution kinetics of calcined ulexite using various leach reagents was examined in recent years [13,15,17,22,24,34].

In this study, the dissolution of calcined ulexite at different dehydration temperatures was investigated in ammonium acetate solutions. The effects of calcination temperature, solution concentration, reaction temperature, solid to liquid ratio, and stirring speed on the dissolution of calcined ulexite were examined.

2 Experimental

2.1. Material

The ulexite sample used in the study was provided from Kırka, Eskişehir, Turkey. The sample was crushed, ground, and then sieved using standard test sieves to obtain different particle sizes. A fraction of 0.425−0.850 mm size was used in the calcination process. The original ore sample (uncalcined) was analyzed, and it was determined that the mineral contained 42.08% B_2O_3, 13.94% CaO, 7.85% Na_2O, 35.96% H_2O, and 0.17 % insoluble matter. The XRD pattern of the sample is given in Fig. 1.

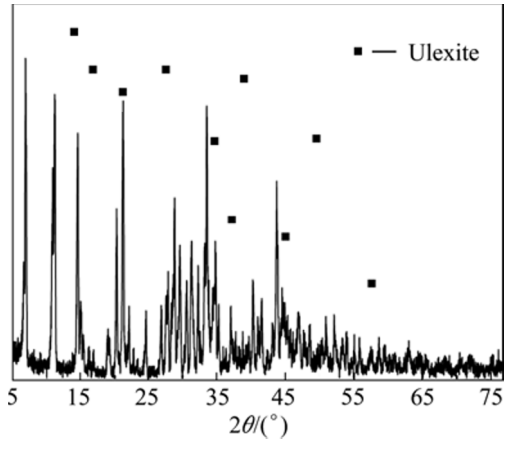

Fig. 1 XRD pattern of original (uncalcined) ulexite sample

2.2 Method

Ulexite dehydration was performed isothermally in an oven at constant temperatures of 100−250 °C for 3 h. The aim of dehydration process essentially was to obtain calcined ulexite samples for use in the determination of the relationship between solubility and calcination. After putting 2 g of the sample with particle size of 0.425−0.850 mm in a ceramic crucible furnished with a cover, the sample was subjected to a given temperature. Following this procedure, the sample was cooled and weighed. Thus, calcination data of samples at various temperatures were obtained.

The dissolution experiments were performed in a 500 mL cylindrical glass reactor equipped with a mechanical stirrer, a reaction temperature control unit, and a condenser to avoid loss of solution by evaporation. The experimental procedure was initiated by adding 200 mL ammonium acetate solution into the glass reactor and bringing it to the desired reaction temperature. A given amount of calcined solid sample was then added to the solution. The dissolution process was carried out for various reaction time. 3 mL liquor were withdrawn at regular intervals during the reaction and were immediately filtered. The amount of dissolved calcium in the solution was determined complexometrically using TitriplexIII solution as titrant. The conversion fraction (x) of calcined ulexite was calculated.

In the dissolution experiments, the effects of calcination temperature, concentration of ammonium acetate solution, reaction temperature, solid to liquid ratio, and stirring speed were investigated.

3 Results and discussion

During the thermal treatment, ulexite loses some hydrate water depending upon the dehydration temperature. The dehydration reaction of ulexite can be written as follows:

$$Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O_3(s)\longrightarrow Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}nH_2O(s)+(16-n)H_2O(g) \quad (1)$$

where n is the mole number of water remaining after dehydration. Relationship between the mass loss and B_2O_3 content by calcination process is given in Fig. 2. It can be seen from Fig. 2 that the B_2O_3 content increases with increasing mass loss as the calcination temperature arises. At temperature higher than 200 °C, the mass loss was not significant.

When the calcined ulexite is added into ammonium acetate solution, the overall reaction occurring during the dissolution process is probably as follows:

$$Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}nH_2O(s)+6NH_4CH_3COO(aq)+(12-n)H_2O(l)\longrightarrow 2NaCH_3COO(aq)+2Ca(CH_3COO)_2(aq)+6NH_3(aq)+10H_3BO_3(aq) \quad (2)$$