Journal of Industrial and Engineering Chemistry 20 (2014) 2727–2734

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Characteristics of precipitated calcium carbonate by hydrothermal and carbonation processes with mega-crystalline calcite using rotary microwave kiln

Dae Ju Hwang [a], Jae Yong Ryu [b], Young Hwan Yu [a], Kye Hong Cho [a], Ji Whan Ahn [c], Choon Han [d,*], Jong Dae Lee [e]

[a] Korea Institute of Limestone and Advanced Materials, Chungbuk 395-903, Republic of Korea
[b] Ulimeng Co., Ltd, Chungbuk 373-809, Republic of Korea
[c] Korea Institute of Geoscience and Mineral Resources 305-350, Republic of Korea
[d] Department of Chemical Engineering of Kwangwoon University, Seoul 139-701, Republic of Korea
[e] Department Chemical Engineering of Chungbuk National University, Chungbuk 361-763, Republic of Korea

ARTICLE INFO

Article history:
Received 28 June 2013
Accepted 27 October 2013
Available online 9 November 2013

Keywords:
Mega-crystalline calcite
Calcination
Rotary microwave kiln
Carbonation
Hydrothermal

ABSTRACT

In the conventional kiln, mega-crystalline calcite (m-CC) breaks apart easily during calcinations, and cannot be easily converted to CaO due to that it requiring a lot of heat. In this study, m-CC was calcined to CaO of around 1 mm using the rotary microwave kiln. Furthermore, $CaCO_3$ was produced by the carbonation process and hydrothermal process, and the form of $CaCO_3$ was characterized.

Calcination of m-CC using the rotary microwave kiln resulted in CaO (97 wt%) of relatively fine size. $CaCO_3$ of colloidal-shaped and 6 μm in size could be prepared by applying the carbonation process to $Ca(OH)_2$ using a bubble reactor at 25 °C. As the carbonation temperature increased from 25 to 80 °C, the shape of prepared $CaCO_3$ changed from a colloidal-type to spindle-type of 1 μm due to self-assembly. Also, hexagonal-shaped aragonite could be prepared by the hydrothermal process with the supersaturated $Ca(HCO_3)_2$ solutions.

1. Introduction

Carbonate minerals are classified into various types such as calcite, limestone, dolomite, etc. Among carbonate minerals, limestone is theoretically composed of CaO 56 wt% and CO_2 44 wt%. However, natural limestone used for calcination has a CaO content of 53–55 wt% or more with SiO_2, MgO, Fe_2O_3 and Al_2O_3 as impurities by 1–3 wt% [1,2,4].

Calcination is thermal decomposition of carbonate minerals ((Calcite ($CaCO_3$), limestone ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) to produce CaO. Most lime kilns for calcinations of carbonate minerals are normal shaft kiln, double-inclined kiln, multi-chamber kiln, annular shaft kiln, rotary kiln and mixed-feed shaft kiln [3].

Calcite, a form of carbonate minerals, is thermally unstable in spite of high CaO content. Especially, m-CC breaks apart very easily and cannot be calcined in conventional shaft or rotary kilns because such kilns usually demand 25 mm of minimum size for calcinations. Calcination characteristics of m-CC in an electrical furnace and a batch type microwave kiln were previously investigated by us [2,4,16]. In that study, it was found that only one eighth calcination time was needed for the calcinations of m-CC at 950 °C in the microwave kiln compared to the electrical furnace. Furthermore, spindle-typed $CaCO_3$ could be prepared through the carbonation process at 60 °C using CaO obtained in an electrical furnace. On the other hand, the same $CaCO_3$ could be prepared at 40 °C using CaO obtained in a microwave kiln [4].

As for methods to synthesize $CaCO_3$, the carbonation process ($CaO–H_2O–CO_2$ system), or the soda process ($CaCl_2–Na_2CO_3$ system) are used. CaO is important during hydration and carbonation reactions in the $CaO–H_2O–CO_2$ system. Various types of CaO can be produced depending on gemstone purity, size and lime kiln type [4]. Although limestone is theoretically composed of CaO 56 wt% and CO_2 44 wt%, the gemstones collected from nature normally contain 1–3 wt% impurities, which bring difficulties in controlling the crystal phase and shape during $CaCO_3$ synthesis in the $CaO–H_2O–CO_2$ system [4–7]. The $CaO–H_2O–CO_2$ system of three phases, solid, liquid and gas, has a difficult carbonation

---

[*] Corresponding author. Tel.: +82 113580667; fax: +82 29090667.
E-mail address: chan@kw.ac.kr (C. Han).

http://dx.doi.org/10.1016/j.jiec.2013.10.061

mechanism compared with the $CaCl_2$–Na_2CO_2 system, as well as difficulty in controlling the crystal phases [8,9]. Also, the aragonite crystal phase of hollow and tubular-shaped $CaCO_3$ is synthesized by the hydrothermal process, and may be synthesized according to the method of feeding the supersaturated solution of $CaCO_3$ [14,15].

In this study, CaO conversion was induced by calcining domestically mined m-CC among carbonate minerals in a rotary microwave kiln (RMK). Then, $CaCO_3$ was prepared through the carbonation and hydrothermal process with CO_2 and supersaturated solution effects by hot water was investigated. After using the synthesized colloidal-shaped $CaCO_3$ (25 °C) to produce the supersaturated solution, supersaturated solution was added to hot water for the preparation of the hexagonal-shaped, aragonite $CaCO_3$.

2. Experimental

2.1. Materials and characterization

In order to fractionize calcite, calcite from Sungji-lime Co. Ltd., Korea was used as the raw material for this study. Calcite was crushed to 25–30 mm in size with the use of a hammer mill, and then was pulverized to 1 mm or less in size with a jaw crusher.

For the analysis, calcite crystals were analyzed by X-ray diffraction (XRD; model: D/MAX2500 V/PC, Rigaku, Japan). Previously, qualitative analysis was conducted by the XRD method. Therefore, the XRD patterns of unknown material were compared with those of standard materials for identification. On the other hand, quantitative XRD analyses could be recently possible by employing the international center for diffraction data (ICDD) card and programming. By using the ICDD card in the XRD method, the information on unknown materials (2Θ, diffraction intensity, Miller Index, etc.) can be checked for identification and quantitative weight percent of the material can be calculated.

Inorganic components (CaO, SiO_2, MgO, Fe_2O_3, Al_2O_3) of the calcite were analyzed by XRF (model: ZSX Primus II, Rigaku, Japan). The whiteness of synthesized $CaCO_3$ was measured by the whiteness analyzer (model: X-Rite Premier 8400, X-RITE, USA). In addition, the microscopic structures and shapes of CaO, and $CaCO_3$ were analyzed with the use of FE-SEM (model: S-4300, HITACHI, Japan).

2.2. Syntheses of $CaCO_3$

Using RMK (Ulimeng, Ltd., Korea), calcite was calcined (Fig. 1). Major construction and structural characteristics of RMK, and calcinations and operation characteristics of carbonate minerals were reported by Hwang et al. [16]. They described major construction characteristics of RMK and the calcinations characteristic according to the feeding amount of the calcined material. In our study, the rotation angle was maintained as 3°, and SiC (purity 98%, t = 15 mm, L = 1000 mm) tube was used for heating. RMK was equipped with a magnetron (LG electronics Co., Ltd., Korea, model: 2M290 (2.45 GHz, 3.0 kw, water cooling type (2ea) and air cooling type (2ea)), 4ea), and magnetron power supply (Ulimeng Co., Ltd., Korea, model: SMPS-4500 (3 kw full bridge switch), 4ea). For heat insulation, Al_2O_3 insulation boards (t = 50 mm) were used. The rotation speed was controlled by a rotation deceleration motor with the rotation speed at 12 cycle/min. The feeding was controlled by a screw feeder, 0–10 steps. M-CC (feed amount: 8 kg, particle size: 1.18–0.85 mm) was fed at the rate of (a) 1 kg/h, (b) 1.5 kg/h, (c) 3 kg/h and (d) 4.5 kg/h. The feed was calcined for 30 min at 950 °C (heating rate: 20 °C/min).

$CaCO_3$ was synthesized with the use of a reactor shown in Fig. 2. For synthesis, a G3 glass filter with porosity of 16–40 μm was used as a bubble plate, and CO_2 gas was fed at a rate of 200 cc/min after putting $Ca(OH)_2$ (0.3 M) into the reactor. To find out temperature effects, synthesis was performed at the temperatures of 25 °C, 40 °C, 60 °C and 80 °C. In the carbonation process, pH values were 12.7 (25 °C), 12.3 (40 °C), 11.8 (60 °C) and 11.3 (80 °C), and the times to finish the reaction at pH 6.0 were 30 min, 20 min, 20 min and 10 min, respectively.

For hydrothermal process, synthesized colloidal-shaped $CaCO_3$ was used, and to produce supersaturated solution, colloidal-shaped $CaCO_3$ 0.1 M was placed in the reactor and CO_2 flow rate

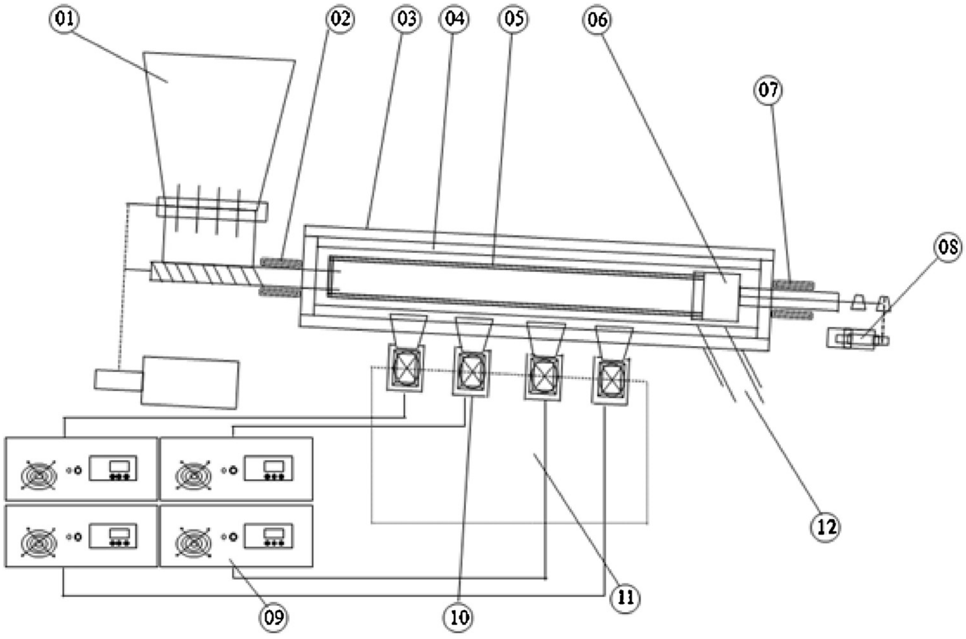

Fig. 1. Scheme of the rotary microwave kiln: 01, screw feeder; 02, inlet cover section; 03, cavity; 04, insulation (ceramic board); 05, heating elements (SiC); 06, refractory (Al_2O_3 99.7%); 07, shaft cover section; 08, heating elements rotation deceleration motor; 09, D.C power supply; 10, microwave generator (Magnetron); 11, chiller and piping; 12, outlet cover section.