Multiple model approach to evaluation of accelerated carbonation for steelmaking slag in a slurry reactor

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HIGHLIGHTS

- The effect of reaction time, temperature and L/S ratio on conversion was evaluated.
- CO_2 mass balance in slurry reactor was established with an error of less than 10%.
- Reaction kinetics and effective diffusivity for carbonation were determined by SCM.
- The maximum conversion was predicted by RSM via nonlinear mathematical programming.
- Applications and limitations of SCM and RSM for BOFS carbonation were illustrated.

ARTICLE INFO

ABSTRACT

Basic oxygen furnace slag (BOFS) exhibits highly alkaline properties due to its high calcium content, which is beneficial to carbonation reaction. In this study, accelerated carbonation of BOFS was evaluated under different reaction times, temperatures, and liquid-to-solid (L/S) ratios in a slurry reactor. CO_2 mass balance within the slurry reactor was carried out to validate the technical feasibility of fixing gaseous CO_2 into solid precipitates. After that, a multiple model approach, i.e., theoretical kinetics and empirical surface model, for carbonation reaction was presented to determine the maximal carbonation conversion of BOFS in a slurry reactor. On one hand, the reaction kinetics of BOFS carbonation was evaluated by the shrinking core model (SCM). Calcite ($CaCO_3$) was identified as a reaction product through the scanning electronic microscopy and X-ray diffraction analyses, which provided the rationale of applying the SCM in this study. The rate-limiting step of carbonation was found to be ash-diffusion controlled, and the effective diffusivity for carbonation of BOFS in a slurry reactor were determined accordingly. On the other hand, the carbonation conversion of BOFS was predicted by the response surface methodology (RSM) via a nonlinear mathematical programming. According to the experimental data, the highest carbonation conversion of BOFS achieved was 57% under an L/S ratio of 20 mL g^{-1}, a CO_2 flow rate of 0.1 L min^{-1}, and a pressure of 101.3 kPa at 50 °C for 120 min. Furthermore, the applications and limitations of SCM and RSM were examined and exemplified by the carbonation of steelmaking slags.

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1. Introduction

Recently, scientists have found that an increase of greenhouse gas in the atmosphere enhances global warming (Cubasch et al., 2013). The global mean surface temperature rose 0.075 ± 0.013 °C per decade from 1901 to 2012, while the concentration of carbon dioxide (CO_2) in the atmosphere increased from 275 to 391 ppm

over the past 250 years (Hartmann, 2013). Therefore, carbon capture, utilization and storage (CCUS) become one of the critical strategies that retard the rate of CO_2 discharge. There are numerous carbon capture methods developing by different groups, such as chemical and physical absorption (Yu et al., 2012), gas-separating membranes (Klemeš et al., 2007), and mineralization (Pan et al., 2012). Among CCUS methods, CO_2 mineralization appears to be an environmentally friendly alternative for both CO_2 capture and storage because it can not only reduce the CO_2 emission but also convert CO_2 to stable precipitates (Sanna et al., 2014). The energy for formation of gaseous CO_2 (i.e., -400 kJ mol^{-1}) can decrease to around -1100 kJ mol^{-1} as solid $CaCO_3$ precipitates (Brady, 1996). It has been demonstrated that the mineralization process using natural ores or industrial solid waste is superior in providing higher storage capacity and longer storage time (Seifritz, 1990; Lackner, 2003; Bobicki et al., 2012). According to the report by Lackner (2003), although there are natural ores on Earth to sequester the CO_2 emissions from all fossil fuels, cost-effective methods for accelerating carbonation are required to develop.

Industrial solid wastes, such as steelmaking slag, are relatively cheaper feedstock than natural ores. Therefore, CO_2 fixation capacity of steelmaking slag through carbonation process has been evaluated (Bonenfant et al., 2008; Teir, 2008; Pan et al., 2013b; Santos et al., 2013). Since steelmaking slag is chemically unstable with high calcium content, it can be readily hydrated and reacted with CO_2 to form carbonates (Lekakh et al., 2008). For instance, the fraction of calcium leaching from steelmaking slag was 97%, when acetic acid was used as extractant (Eloneva et al., 2012). In addition, a carbonation conversion of 80% was achieved by using steelmaking slag with a particle size less than 38 μm under a pressure of 1.0 MPa at 200 °C for 15 min (Huijgen et al., 2006). Beside the studies of leaching and carbonation behaviors for steelmaking slag, different novel approaches, such as two-step pH swing (Mattila et al., 2012), are developed to produce pure calcium carbonate precipitates for further utilization.

Identifying the effect of key operating factors on carbonation performance is crucial to reaction design and system optimization. There are several theoretical models available for evaluating the performance of carbonation using a CaO-based material, such as random pore model (Bhatia and Perlmutter, 1983), overlapping grain model (Liu et al., 2012), shrinking core model (Lekakh et al., 2008), and surface coverage model (Pan et al., 2014). For the sake of simplicity, different assumptions were made by each model to avoid complicate calculation. This study presents a multiple model approach, i.e., theoretical kinetics and empirical mathematical equation, to determining the maximal carbonation conversion of BOFS in a slurry reactor. The objectives of this research were (1) to evaluate the effect of various operating factors, i.e., reaction temperature, liquid-to-solid (L/S) ratio and reaction time, on the carbonation conversion of BOFS in a slurry reactor; (2) to determine the reaction kinetics and rate-limiting step by applying a shrinking core model (SCM); (3) to predict the carbonation performance by response surface methodology (RSM) using a nonlinear optimization program; and (4) to examine the applications and limitations of SCM and RSM exemplified by the carbonation of steelmaking slags.

2. Materials and methods

2.1. Materials

The ground BOFS was provided by the China Hi-ment Corporation (Kaohsiung, Taiwan). The ground BOFS was sieved by a standard sieve with mesh #325 (i.e., < 44 μm). After sieving, BOFS samples were placed in an oven at 105 °C to eliminate surface

moisture and then collected in an air-tight bag. Deionized (DI) water (18.2 MΩ cm^{-1}) was produced by the Water Still Apparatus (Chemist, A4DL, Taiwan). In addition, high-pressure CO_2 with 99% purity was supplied by Ch'ing-Feng Gas Corporation (Taipei, Taiwan).

2.2. Experiment

Fig. S1 (see Supporting Information) shows a schematic diagram of the slurry reactor system used for the BOFS carbonation. The slurry reactor was a glass column 0.20 m in height and 0.08 m in diameter, and the sampling port was located 0.02 m above the bottom of the reactor. Different amounts of fresh BOFS samples were mixed with 250 mL of DI water in the slurry reactor. According to the previous study (Chang et al., 2011), the CO_2 flow rate was set at 0.1 L min^{-1} under atmospheric pressure by a mass flow controller (MC-1SLPM-D, Alicat Scientific Inc., USA) for providing sufficient mass transfer rate of CO_2 in the slurry within the similar size of reactor. The reaction temperature was automatically controlled by a stirring and heating plate (PC-420D, Corning, Mexico).

To evaluate the effect of operating factors on carbonation performance in a slurry reactor, a response surface was introduced using the response surface methodology (RSM) coded with Design Expert 8.0 software (Stat-Ease, Inc., USA). The operating factors for the slurry reactor system considered in this study include reaction temperature (i.e., 30, 40, 50, 60 and 70 °C), L/S ratio (i.e., 5, 10 and 20 mL g^{-1}), and reaction time (i.e., 5, 10, 20, 40, 60 and 120 min). These factors, i.e., temperature, L/S ratio, and reaction time, were coded as high ($+1$) and low (-1) levels in the RSM.

2.3. Characterization of BOFS

The composition of fresh BOFS was analyzed at the Chemistry Analysis Laboratory in China Hi-ment Corporation, Kaohsiung, Taiwan. Acetic acid and phosphoric acid were used for digesting various ingredients in BOFS samples. A micro-digestion method was applied at high temperature and pressure to ensure completely dissolution of BOFS samples. The concentrations of various metal ions in the extracted solution were measured by an inductively coupled plasma optical emission spectroscopy (ICP-OES).

After carbonation, the reacted BOFS slurry sample was filtered with a 0.45 μm membrane to separate the solid and liquid phases. The solid sample was then dried in an oven at 105 °C for 1 d to completely remove moisture. The dried BOFS samples were analyzed by thermogravimetric analysis (TGA), scanning electronic microscopy (SEM), and X-ray diffraction (XRD). In contrast, the concentrations of metal ions in the filtrate (i.e., liquid phase) were measured with an atomic absorption spectrometer (AAS, PerkinElmer AA800, USA). In addition, the concentration of total inorganic carbon (TIC) in the liquid phase was determined using an Aurora 1030W TIC Analyzer (O.I. Analytical, Canada).

The surface micro-structure of the BOFS samples before and after carbonation was analyzed by SEM (Hitachi S-800, Tokyo, Japan). In addition, XRD (X' Pert Pro, PANalytical, Almelo, The Netherlands) was applied to identify and characterize crystalline materials using monochromatic X-rays. The XRD patterns of a BOFS sample before and after the carbonation reaction were collected from 20° to 80° with a scanning time of 1 s per step.

2.4. Determination of carbonation conversion of BOFS using thermal analysis

TGA (TGA-51, Shimadzu, Kyoto, Japan) was used to determine the carbonation conversion of BOFS before and after carbonation. A