Validating carbonation parameters of alkaline solid wastes via integrated thermal analyses: Principles and applications

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HIGHLIGHTS

- Key carbonation parameters of wastes are determined by integrated thermal analyses.
- A modified TG-DTG interpretation is proposed, and validated by the DSC technique.
- The modified TG-DTG interpretation is further verified by DTA, TG-MS and TG-FTIR.
- Kinetics and thermodynamics of $CaCO_3$ decomposition in solid wastes are determined.
- Implication to maximum carbonation conversion of various solid wastes is described.

GRAPHICAL ABSTRACT
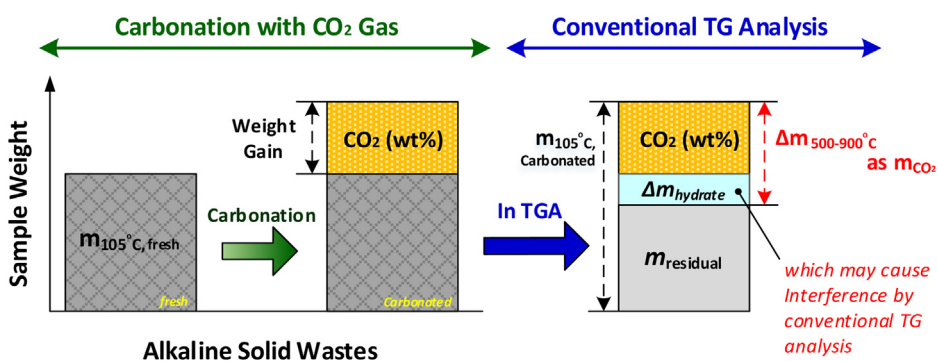
ABSTRACT

Accelerated carbonation of alkaline solid wastes is an attractive method for CO_2 capture and utilization. However, the evaluation criteria of $CaCO_3$ content in solid wastes and the way to interpret thermal analysis profiles were found to be quite different among the literature. In this investigation, an integrated thermal analyses for determining carbonation parameters in basic oxygen furnace slag (BOFS) were proposed based on thermogravimetric (TG), derivative thermogravimetric (DTG), and differential scanning calorimetry (DSC) analyses. A modified method of TG-DTG interpretation was proposed by considering the consecutive weight loss of sample with 200–900 °C because the decomposition of various hydrated compounds caused variances in estimates by using conventional methods of TG interpretation. Different quantities of reference $CaCO_3$ standards, carbonated BOFS samples and synthetic $CaCO_3$/BOFS mixtures were prepared for evaluating the data quality of the modified TG-DTG interpretation, in terms of precision and accuracy. The quantitative results of the modified TG-DTG method were also validated by DSC analysis. In addition, to confirm the TG-DTG results, the evolved gas analysis was performed by mass spectrometer and Fourier transform infrared spectroscopy for detection of the gaseous compounds released during heating. Furthermore, the decomposition kinetics and thermodynamics of $CaCO_3$ in BOFS was evaluated using Arrhenius equation and Kissinger

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equation. The proposed integrated thermal analyses for determining CaCO$_3$ content in alkaline wastes was precise and accurate, thereby enabling to effectively assess the CO$_2$ capture capacity of alkaline wastes for mineral carbonation.

1. Introduction

Recently, interest in the accelerated carbonation of alkaline solid wastes (e.g., steelmaking slags) has sharply escalated due to their potential to fix gaseous CO$_2$ from industry into solid precipitation (e.g., calcium carbonate), that could mitigate global climate change [1–4]. Moreover, the physico-chemical properties of solid wastes can be improved by carbonation, thereby increasing the potential for being used as construction materials such as supplementary cementitious materials and/or aggregates in civil engineering [5]. To evaluate and compare the performance of accelerated carbonation provided by various types of approach and process, thermo-analytical techniques, including thermogravimetric (TG) analysis, derivative thermogravimetric (DTG), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) have commonly been utilized to quantify carbonation products such as calcium carbonate (CaCO$_3$) in solid wastes. Other analytical techniques, such as reference intensity ratio method [6] and Rietveld refinement [7] using X-ray diffraction, can also provide quantitative analysis on the carbonate products in solid wastes. Although X-ray techniques can provide precise and accurate information on the fraction of crystal phases, they are generally time-consumed in sample preparation and data processing.

TG analysis was considered as a rapid and accurate method for the determination of crystalline CaCO$_3$ content in highly pure samples [8]. However, in the case of cementitious materials such as concrete and cement [9], it was difficult to realize accurate quantitative profiles of CaCO$_3$ content using only TG data because (1) the way to interpret TG curves for CaCO$_3$ decomposition in a material was varied among researchers; and (2) the temperature ranges of thermal decomposition of CaCO$_3$ overlap the calcareous and hydrated components in these materials. Similar challenges were observed for carbonation of alkaline solid wastes such as basic oxygen furnace slag (BOFS) because their physico-chemical properties are similar to those of cementitious materials.

Two of the most commonly used methods for determining the weight loss of a certain material by interpreting TG curve were (1) delta-Y and (2) on-set methods, as shown in Fig. 1. The delta-Y method is to determine the difference of sample weight directly between two specific temperatures (e.g., T_1 and T_2 in Fig. 1), while the on-set method is to extend the straight line portions of the baseline and the linear portion of the upward/downward slope, mark their intersection, and determine the weight difference between these two intersections. It is noted that there is a significant difference in the determined weight loss for the same TG plot. In particular, in the case of BOFS, the dehydration of calcium silicate hydrates, calcium aluminate hydrates, and other minor hydrates was found to occur between 105 and 1000 °C, resulting in a continuous and steady weight loss [10]. Although it is especially pronounced at temperatures less than 500 °C, consideration must be given to weight loss due to dehydration of the above materials at 500–900 °C. Otherwise, the CaCO$_3$ contents in BOFS will be overestimated by the conventional delta-Y or on-set methods.

Table 1 summarizes the analytical conditions of TG and temperature ranges of the thermal decomposition of Ca(OH)$_2$, MgCO$_3$, and CaCO$_3$ contained in different solid wastes, such as steelmaking slags, coal combustion fly ash, cement kiln dust, and municipal solid wastes, in the literature. As noticed by Table 1, the evaluation criteria of carbonate products by TG analysis were quite different among the literature because of the wide variance in determining the temperature ranges of product decomposition. This is also largely due to the various ways to interpret TG curve, thereby resulting in different bases on performance evaluation of CO$_2$ capture capacity for carbonation. Thus, a validated method needs to be developed for accurately quantifying the CaCO$_3$ content in solid wastes.

In this investigation, a method determining carbonation parameters in alkaline solid wastes via integrated thermal analysis was developed and evaluated, as presented in Fig. 2. The integrated thermal analyses were performed based on TG, DTG and DSC analyses, in conjunction with a mass spectrometer (MS) and Fourier transform infrared spectroscopy (FTIR). A modified method of TG-DTG interpretation was proposed by considering the consecutive weight loss of sample with 200–900 °C due to the decomposition of various hydrated compounds. The objectives of this study were (1) to determine the CaCO$_3$ content in BOFS by modified interpretation using both TG and DTG curves, (2) to validate the data quality of the TG-DTG method via DSC technique; (3) to verify the TG-DTG results by the supporting evidence of qualitative observation, including DTA, TG-MS and TG-FTIR; and (4) to elucidate kinetic and thermodynamic behaviors of CaCO$_3$ decomposition in BOFS based on the Arrhenius equation, Kissinger equation, and transition state theory (see Appendix A).

2. Materials and methods

2.1. Materials

The fresh BOFS was provided by a steelmaking company (Kaohsiung, Taiwan). The as-received BOFS was carbonated with pure CO$_2$ gas via a rotating packed bed under mild conditions [2,5]. According to our previous report [5], the BOFS was rich in CaO ($\sim$48.2%), Fe$_2$O$_3$ ($\sim$26.0%) and SiO$_2$ ($\sim$8.6%). The main crystal phases of the fresh BOFS include brownmillerite (Ca$_2$Fe$_{1.014}$Al$_{0.986}$O$_5$), portlandite (Ca(OH)$_2$), wollastonite (CaSiO$_3$), β-larnite (Ca$_2$SiO$_4$), α-dicalcium silicate hydrate (Ca$_2$(HSiO$_4$)(OH)) and wustite (FeO). More details on the physico-chemical properties of BOFS can be found in our previous study [5].

In this study, three levels of carbonation degree of BOFS, i.e., low ($\sim$20%), medium ($\sim$50%), high ($\sim$90%), were selected for analytical tests. To generate the calibration (or standard) curve, the synthetic CaCO$_3$/BOFS mixtures were prepared by mixing different amounts of reference CaCO$_3$ powder (i.e., with a purity of 100%, purchased from J.T. Baker 1288-01 (NJ, USA)) with carbonated BOFS. Since the measured particle size of CaCO$_3$ after carbonation was 1–3 μm [2,5], the physico-chemical properties of the reaction product could be similar to the purchased reference CaCO$_3$.

2.2. Thermal analysis techniques

In TG analysis, the weight of sample at different temperatures was recorded under an assigned heating programs. By taking numerical derivation of the TG curve, a DTG plot can be obtained to provide the information on the temperature at the maximum peak and other important peak parameters. In a DSC, a sample cell and a