A study of thermal decomposition of phases in cementitious systems using HT-XRD and TG

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HIGHLIGHTS

- This study suggests correct decompositional temperatures of cementitious phases.
- DTG peaks of a phase can be affected by the presence of other phases.
- In TG, when $Ca(OH)_2$ plentifully exists, the weight of $CaCO_3$ can be overestimated.
- The gas type in TG (N_2 vs. air) had no significant influence on TG below 800 °C.
- Different heating rates and sample fineness can alter the TG results.

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ABSTRACT

Significant variations have been reported on the temperature range of thermal decomposition of cementitious phases. Thus, this study identified temperature ranges on the phases in actual cementitious systems (portland cement (OPC) pastes, blended pastes of ground granulated blast furnace slag (GGBFS) with OPC, and $Ca(OH)_2$-activated GGBFS) by simultaneously using thermogravimetry (TG) and high-temperature X-ray diffraction (HT-XRD) as follows: (1) 81°–91 °C for dehydration of ettringite, (2) ~80°–240 °C for major dehydration of C-S-H, (3) ~241°–244 °C for hydrogarnet, (4) ~129°–138 °C for Al_2O_3-Fe_2O_3-mono phase (AFm), (5) ~411°–427 °C for $Ca(OH)_2$, and (6) ~648°–691 °C for $CaCO_3$. The CaO layers and SiO_2 chains of C-S-H likely started to decompose from 615°–630 °C, and eventually transformed to new crystalline phases. This study also demonstrated that (a) the quantity of calcite could be overestimated due to additional carbonation when $Ca(OH)_2$ is plentifully present in samples, and (b) the quantification of phases would be greatly affected by sample particle size when GGBFS is used in the system.

1. Introduction

Thermogravimetry (TG) and X-ray diffraction (XRD) are commonly used together to identify and quantify cementitious phases (e.g., hydration products of portland cement) [1–4] as these techniques are mutually supportive given that (1) TG enables the quantification of non-crystalline phases (e.g., calcium silicate hydrate (C-S-H)), since each cementitious phase has a characteristic temperature range in its thermal decomposition, and (2) XRD distinguishes cementitious phases that have overlapping temperature ranges of thermal decomposition in TG (e.g., C-S-H vs. ettringite ($C_3A \cdot 3CaSO_4 \cdot 32H_2O$)). In addition, although Rietveld refinement on powder XRD patterns may also allow the quantification of cementitious phases, it requires a significantly high resolution of the XRD patterns [5] as well as a fully resolved crystalline structure for every phase involved [6]. For these reasons, TG and its differential form (DTG) are actively applied to cementitious systems in combination with XRD.

However, as shown in Table 1, earlier studies have reported diverse temperature ranges even for identical phases [7,9–19]; for instance, ettringite showed a large temperature variation in previous studies. In particular, earlier TG studies on pure cementitious phases (e.g., calcite, ettringite) [9,11,14] always reported significantly higher decomposition temperature ranges than those of

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Table 1
Reported decomposition temperature ranges in TG for cementitious phases.

Phases	Temperature range (°C)	Phases	Temperature range (°C)
Ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$)	80 [7] ~100 [8] 125–130 [9]	Hydrogarnet ($Ca_3Al_2(SiO_4)_{3-y}(OH)_{4y}$, $0 \leq y \leq 3$)	250–300 [10] ~325 [11] 250–310, 450–550 [9]
Gypsum ($CaSO_4 \cdot 2H_2O$)	80–220 [12] 100–200 [13] 110–145 [14] 380–450 [15] ~100–140 [8]	Calcium hydroxide ($Ca(OH)_2$)	410–450 [7,14] 430 [16] 450–550 [17] ~510 [18] ~460 [8]
C-S-H	40–60 [14] 50–500 [16] 50–600 [8] 120 [16,19]	Calcite ($CaCO_3$)	520–730 [14] 650–900 [7] 675, 950 [15]

the same phases formed in real cementitious systems. As most of the current studies in the cement and concrete fields have referred to those earlier studies for the phase identification of TG data, this inconsistency may lead to a significant risk of misinterpretation of TG/DTG data.

In addition, although influential factors (e.g., the gas environment of TG, the heating rate of TG, or the particle size of sample) on TG results have been studied in other fields [20], there have been very few studies on these factors in real cementitious systems.

High-temperature X-ray diffraction (HT-XRD) may provide useful information on the thermal behavior of various phases in cementitious systems, as it measures XRD patterns of samples at controlled high temperatures. In particular, HT-XRD identifies the phase transitions of crystalline phases as a function of temperature, and it detects the formation of new phases in high temperatures, which cannot be seen at room temperature in conventional XRD. These transitions and new phase formations would affect the TG/DTG curves in high temperature ranges. In other academic fields, the combination of TG/DTG and HT-XRD has been a common approach to understand thermal transformation and decomposition in complex systems [21,22], but it was not often used in the field of cement and concrete.

The present study attempted to clarify the above concerns on TG/DTG by applying TG and HT-XRD to three different cementitious systems: (1) portland cement paste, (2) ground granulated blast furnace slag (GGBFS)-blended cement paste, and (3) Ca(OH)$_2$-activated GGBFS binder. Subsequently, the influences of the gas environment, heating rate, and sample particle size on TG/DTG curves were investigated, and then these TG/DTG data were compared with HT-XRD results, taken at specifically elevated temperatures. The comparison allowed the identification of the correct temperature ranges of thermal decomposition as well as an understanding of the phases of thermal decomposition.

2. Materials and experiments

OPC and GGBFS were obtained, and synthetic calcite was made from the reaction of CaO with CO$_2$ for this study. The oxide compositions of OPC, GGBFS and synthesized calcite were obtained from X-ray fluorescence (XRF), as presented in Table 2. The OPC and GGBFS used in the present study had general compositions [9,23].

Weight percentages of unburnt carbon in OPC and GGBFS, measured by elemental analyzer, were 0.77 and 0.60 wt%, respectively.

Powder XRD patterns were taken at room temperature using an X-ray diffractometer for the OPC, GGBFS, and synthesized calcite, as shown in Fig. 1. The OPC consisted of tricalcium silicate (C$_3$S), dicalcium silicate (C$_2$S), tricalcium aluminate (C$_3$A), tetracalcium aluminoferrite (C$_4$AF), gypsum (CaSO$_4$·2H$_2$O), and periclase

(MgO), which are common phases in a general OPC, while the GGBFS had only an amorphous phase with calcite. The XRD of the synthesized calcite showed only calcite peaks.

The raw GGBFS and synthesized calcite were subjected to TG to investigate the difference in decomposition temperature between the two different states of calcites (i.e., a pure synthetic form vs. an impurity in raw GGBFS). TG was conducted under the identical experimental conditions and the results are presented in Section 3.1.1.

Three different types of basic mixtures were prepared: (1) OPC paste (denoted PC), (2) GGBFS-blended OPC paste (denoted PC-GG), and (3) Ca(OH)$_2$-activated GGBFS paste (denoted GG-CH). The detailed mixture proportions are presented in Table 3. These mixtures were used as basic pastes to prepare powder samples for HT-XRD and TG.

It is worth noting that the raw GGBFS in this study did not contain any gypsum, and thus, for the samples having GGBFS (i.e., PC-GG and GG-CH), gypsum was added to make sufficient ettringite in these samples, because ettringite was one of the major phases under investigation in this study. Note that the added gypsum generally produces ettringite from the reaction of CaO with GGBFS even when no C$_3$A is present in the system [24].

All fresh pastes from Table 3 were cast in 5 × 5 × 5 cm cubic molds and then cured at 23 °C. Each sample was demolded after one day, and then continuously cured for 3, 28, and 56 days before compressive strength tests. Strength tests were conducted using a universal testing machine under a 0.4 mm/min loading speed. The strength developments of the samples are presented in Fig. 2.

Using the fractured pieces collected after compressive strength tests, powder samples were prepared for TG and HT-XRD measurements. As it is known that TG and XRD are generally influenced by the particle sizes of powder samples [25,26], two different particle sizes of powder samples were also prepared. All the fractured samples were first ground using a mechanical grinder for 2 min. The samples without any further grinding were denoted "C" (i.e., coarse sample), while the samples with further grinding were denoted "F" (i.e., fine sample). The further grinding was carried out by hand with a mortar and pestle for more 5 min. While the fine samples were mainly used both for TG and HT-XRD, the coarse samples were subjected only to TG to investigate the influence of particle size on the TG results. Table 4 provides the full list of prepared powder samples and experimental conditions; the letters that precede the numbers (e.g., PC, GG-CH) imply the type of basic mixture; the numbers (e.g., 3, 28, and 56) indicate the curing days; the last letters C and F indicate the overall particle sizes.

The particle sizes of the prepared powder samples, listed in Table 4, were examined with a laser scattering analyzer to estimate the median particle sizes of the samples. The particle size distributions of the prepared samples are shown in Fig. 3.