On the quantitative thermogravimetric analysis of calcite content in hydrated cementitious systems

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Abstract. Calcite is a compound that is present in hydrated cementitious materials when carbonation of portlandite occurs or when limestone constituents are used. The quantification of its content in cementitious systems is then frequently necessary. Thermogravimetry (TG) measures the change in mass of a material (as a function of time) over a temperature range using a predetermined heating rate. It can be applied to estimate calcite content in the hydrated cement system, considering the temperature range at which it decomposes and releases carbon dioxide. However, the quantification is not easy because the onset of this decomposition is a function of many variables. The tangential method over the TG signal or the integration method over the derivative TG curve (DTG) are usually used to discount the background over the temperature range at which calcite decomposes. However, consistent underestimation of compounds is frequently described. The reasons for this are unclear and some hypothesis are discussed in this paper. Additionally, experimental quantitative TG of cement paste and aggregate containing calcite and diluted with low contents of analytical calcite are compared with the expected contents, as a calibration method regarding calcite content in the samples is given to improve the reliability of the results.

Introduction

Thermogravimetry (TG) is a widely applied technique for characterization of hydration products in cementitious systems. During TG the sample is heated while the weight loss is recorded. Calcite content in hydrated cementitious materials is derived from the progression of carbonation of portlandite, or limestone constituents. For the particular case of calcite, TG reflects its decomposition at a particular temperature range. This reaction cause a weight change which is linked with this particular compound. The quantification of calcium carbonate might however show significant differences according to the method applied for this computation from the TG signal.

The thermodynamical basis of quantitative TG (QTG) is based on the decomposition of calcite between 600 and 800°C [1] (Equation 1). However, some amorphous calcium carbonate may partially decarbonate earlier, between 400 and 600°C, forming CaO and calcite [2]. The crystallinity of CaCO₃ also plays a significant role in the temperature at which it decomposes. Data in the literature [3-5] shows that carbonation of cementitious materials leads to sequestration of CO₂ that may form poorly crystallized carbonates. During TG, the decomposition of these compounds occurs earlier and causes gradual mass loss that ends with a more intense peak around 800°C that could be attributed to the decomposition of well-crystallised calcite. Then, the exact temperature for
the decarbonation peak(s) depends on the relative amount of calcium carbonate, proportion of hemi and monocarbonates, and the fineness of carbonates. Also two consecutive overlapping peaks may result from this process. Despite the advantage of mass of CO$_2$ released per unit mass of calcium carbonate not being depended on the various forms in which it can be present, it seems that poorly crystallized compounds might be the main reason for underestimation of calcium carbonate content.

\[
\text{CaCO}_3(s) \rightarrow \text{CaO} (s) + \text{CO}_2 (g)
\]

(1)

The amount of calcite is computed from the corresponding weight loss considering that 100 g of CaCO$_3$ release 44 g of CO$_2$. The main concern is how this weight loss is determined. For this, the tangential method and the integration method are frequently applied.

The tangential method computes the mass loss from the distance between the tangents to the TG curve after and before the change in the slope corresponding to the weight loss step.

Differentiation of the thermogravimetric data, namely derivative thermogravimetry or differential thermogravimetry (DTG), allows a better resolution and identification of consecutive weight losses. Here, the quantification of the weight loss can be obtained from integration of the DTG over a determined temperature range or time period, discounting the background, this is the area over the secant to the curve between the onset and end of the peak. For other thermal analysis such as DTA, the interpretation and quantification of the results can be more difficult due to non stable base line signal caused by the intrinsic properties of the products obtained during the thermal decomposition of the sample. Then, the calcium carbonate decomposition can be better evaluated by DTG than by DTA [6].

It should be mentioned that results of thermal analysis are also strongly influenced by setting up of the measurement (vessel type, heating rate, sample amount, particle size, gas flow rate, purging gas, pretreatments). This make the comparison between data in the literature quite difficult.

In this paper, a procedure for quantification of calcite in cementitious systems is presented. The possible correction for underestimation by the tangential and integration methods is analyzed. Cement pastes and gravel aggregate were tested with and without admixed pure calcite as internal standard. From the results, the resultant quantified amounts are compared with the added amount and correction factors for the systematic underestimation are derived.

**Experimental**

First, pure calcite was analysed by TG, as a procedure for calibration of the device for quantitative analysis. This pure calcite used as reference material was an analytical reagent grade chemical commodity. Next, OPC and OPC+limestone pastes, and siliceous gravel (containing about 15% of carbonate), with and without known amounts of extra calcite added were tested.

The tested pastes were prepared with pure OPC (CEM I 42.5) and OPC+10% limestone powder and cured for 28 days. After the curing period, they were manually ground with mortar and pestle and tested for TG. The difference between the measurements of pure samples, and samples admixed with 5 or 10% of standard calcite, is compared with the added amount of calcite. This comparison was additionally made with samples consisting in a ground gravel aggregate containing carbonates with and without internal standards.

Thermogravimetric analysis were carried out using a Netzsch STA 449F3 apparatus. Samples of approximately 50mg were tested in alumina open crucibles and exposed under an inert atmosphere of nitrogen to increasing temperatures, ranging from 20 °C to 1100 °C at a rate of 10 °C/min.

**Results**

After the measurement, a correction for buoyancy effect is always necessary. This correction signal is obtained by measuring an empty crucible under exactly the same conditions that are used for the analysis of samples. Then, the apparent mass increase due to decreasing gas pressure in the chamber during heating is discounted. However, some little discrepancies are always present, and it
can be seen that the correction using one or another curve will always result in dissimilar results. Making an immediate blank determination before measuring the actual sample is the most appropriate procedure and would normally reduce the effect of this variation in the blank.

In this respect, TG results for calcite are presented in Figures 1 (a) uncorrected and (b) corrected for buoyancy. In Figure 1 (b), the mere weight losses in the ranges 20-105°C, 105-600°C and 105-1000°C are showed. Also, the weight loss by the tangential (Marsh) method is computed for the step corresponding to calcite decomposition. Here, the weight loss of 2.53% observed in the range of 105-600°C is not connected with decomposition of calcite, and cannot be linked with the composition of the material either. Instead, it seems that this reduction is an artifact caused by the correction for buoyancy, which is not completely the same for the blank and the measurement of the samples. This artifact would be relatively higher for smaller amounts of sample being tested. Identifying this issue and choosing a more convenient correction curve is possible in this case, but not for paste samples where this effect overlaps with weight loss from dehydration of C-S-H during the whole temperature interval from 20 to 600°C and no individual distinction is possible. Then, despite a weight loss virtually induced by the correction by the blank, the real extent of this influence cannot be determined. In this sense, a double measurement of the sample with and without an admixed amount of internal standard could give some more clarification on the issue.

![Figure 1. TG measurements for calcite. Blank correction for buoyancy (blue), and calcite (red).](image-url)
Figures 2, 3 and 4 present results with/without added calcite from OPC and OPC+limestone pastes, and gravel aggregate, respectively. For pastes, peaks for DTG around 120, 170, 450 and 750°C are noted in association with decomposition of ettringite, AFm, portlandite and calcite, respectively. All the remaining weight loss is associated with dehydration of C-S-H. Naturally, the inclusion of calcite increases the intensity of the corresponding peak and weight loss step in the TG signal. For the limestone blended paste admixed with calcite, a double peak for calcite is noted, presumably due to differences in crystallinity and grain sizes for calcite from limestone and the calcite added. This difference is not noted in the signals for OPC paste with added calcite. It can also be noted that the addition of calcite causes a change in the position of the peak in the DTG. This shift towards higher temperatures is in accordance with the added amounts.

![Figure 2. TG for limestone blended paste.](image)

LA1A: pure paste; LA1A2810C: paste+10% calcite; LA1A285C: paste+5% calcite.

![Figure 3. TG for OPC paste.](image)

P1: pure paste; P12810C: paste+10% calcite; P1285C: paste+5% calcite.
Discussion

From the weight losses obtained from the tangential and integration methods, the corresponding computed amounts of calcite are presented in Table 1. For samples consisting in calcite and aggregate with/without added calcite, only one decomposition reaction takes place during heating. Then, both methods should theoretically result in the same amount to that obtained from the mere weight loss (i.e. the start and the end parts of the TG signal should be horizontal in the graph), but this is not the case. Moreover, it is notorious that only when the quantification is based on the mere weight loss in the TG of calcite (44.02%), 100% of calcite is obtained. However, when the tangential and integration methods are applied the amount of calcite is underestimated by factor of 0.912 and 0.914, respectively.

The previous values were used as correcting factors applied to determinations on pastes (Table 1). Still, the differences between the measurements with and without added calcite are lower than the actual added amounts. Consequently, there seems to be a source of error additional to that of buoyancy correction, that could not be discerned at this stage.

In all cases, better results are obtained for the integration method in comparison with the tangential method. Although from a mathematical point of view the tangential and integration methods are the same procedure, the method based on the integration over the DTG curve is more precise for low contents, as the absolute local minimums of this curves in the ranges near the onset and end temperatures are easier to be determined than the change in the slope of the TG required for the tangential method. Moreover, the integration method offers a better traceable quantification than the tangent method and is less affected by the noise in the signal.
Table 1. Contents of calcite determined from weight losses from the tangential and integration methods and corrected by factors obtained from the TG of analytical calcite [g/100 g sample].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tangential method</th>
<th>Integration method</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without correction</td>
<td>Corrected</td>
</tr>
<tr>
<td>Standard Calcite</td>
<td>91.23</td>
<td>-</td>
</tr>
<tr>
<td>AGG</td>
<td>13.84</td>
<td>15.17</td>
</tr>
<tr>
<td>AGG5C</td>
<td>18.75</td>
<td>20.55</td>
</tr>
<tr>
<td>AGG10C</td>
<td>22.57</td>
<td>24.74</td>
</tr>
<tr>
<td>P1</td>
<td>1.18</td>
<td>1.30</td>
</tr>
<tr>
<td>P1285C</td>
<td>5.75</td>
<td>6.30</td>
</tr>
<tr>
<td>P12810C</td>
<td>9.93</td>
<td>10.89</td>
</tr>
<tr>
<td>LA1A</td>
<td>6.73</td>
<td>7.37</td>
</tr>
<tr>
<td>LA1A285C</td>
<td>11.00</td>
<td>12.06</td>
</tr>
<tr>
<td>LA1A2810C</td>
<td>14.23</td>
<td>15.59</td>
</tr>
</tbody>
</table>

Conclusions

Increased reliability of the quantification of calcite in hydrated cement pastes when the measurements are compared to those of samples with added calcite is achieved. Still, the amounts obtained for added calcite were systematically underestimated by TG. Among the potential causes of this underestimation, the imperfect correction for buoyancy seems to be responsible for a high proportion of the bias, however, other sources of error still remain unexplained.

Higher accuracy was obtained for quantifications based on the integration over DTG in comparison with the tangential method. The integration method is more precise than the tangential method because the onset is more easily identified by the operator as a difference in the vertical magnitude in the DTG curve rather than as a difference in the angle of the slope in the TG curve. Therefore, traceable and more precise results can be expected from DTG, especially considering that calcite in cementitious materials can show very variable crystallinity and grain size, with an extended range of temperatures for its decomposition.

References