

Calibrated quantitative thermogravimetric analysis for the determination of portlandite and calcite content in hydrated cementitious systems

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Abstract Portlandite and calcite are compounds of interest regarding different processes related to microstructural and durability issues of cementitious materials, such as carbonation, pozzolanic action, and hydration degree. The quantification of their contents in cementitious systems is thus frequently required. Thermogravimetry (TG) measures the change in mass of a material (as a function of time) over a temperature range using a predetermined heating rate. The TG method can be applied with certain success to estimate portlandite and calcite contents in the hydrated cement system, considering the temperature range at which each compound decomposes and releases water or

carbon dioxide, respectively. However, a mature hydrated cement paste contains hydrated calcium silicate, portlandite and calcite phases. The quantification procedure is therefore complicated because of the concurrent interference among them. The tangential method over the TG signal or the integral method over the derivative TG curve is usually used to discount water loss from hydrated calcium silicates over the temperature range at which portlandite and calcite decompose. However, by the use of TG consistent underestimation of portlandite content in hydrated cementitious systems is still described in the literature. Potential causes for this underestimation are analysed in this paper, and a calibration procedure by means of an internal standard is proposed. Cement paste and aggregate samples are analysed. Differences between TG quantifications of these pure samples and those diluted with low contents of internal standards are compared with the added amounts of internal standard. In that way, a calibration method of the device is applied for correction of the actual portlandite and calcite contents in the samples. For this purpose, both analytic quality calcite and freshly prepared portlandite were used as internal standards. The results show that improved quantifications can be achieved with this calibration. Also, calcite seems to be more suitable as internal standard than portlandite as the best outcome was obtained for the first case.

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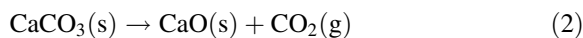
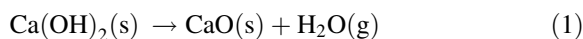
1 Introduction

Thermogravimetry (TG) is a widely applied technique for characterization of hydration products in cementitious systems. Measurements of bound water, calcite and portlandite contents by TG are usually reported and used to assess hydration and reaction of cement and supplementary cementitious materials, as well as carbonation progression [1]. During TG the sample is heated while the weight loss is recorded. TG reflects dehydration, dehydroxylation, decarbonation, oxidation, or decomposition of compounds in the sample. These reactions cause weight changes at certain temperature intervals which are typical for each compound.

The quantification of bound water, portlandite and calcium carbonate might however show significant differences according to the method applied for this computation from the TG signal [1, 2]. A significant issue for the quantification of phases is the overlapping of signals from C–S–H dehydration with portlandite dehydroxylation and calcite decomposition [2]. Then, these processes occur simultaneously during heating, and the contributions to the weight loss must be separated according to the corresponding sources.

The thermodynamical basis of quantitative TG (QTG) is as follows [2]. Portlandite dehydroxylates at approximately 460 °C (Eq. 1). Calcite decomposes between 600 and 800 °C (Eq. 2). Some amorphous calcium carbonate may however partially decarbonate earlier, between 400 and 600 °C, forming CaO and calcite [3]. The sequestration of CO₂ during carbonation of cementitious materials may form poorly crystallized carbonates [4–7], causing the decomposition of these compounds to occur earlier during TG. Thiery et al. [7] indicate that portlandite carbonation precipitates well-crystallised calcite and decomposes at a higher temperature than that for amorphous and metastable calcium carbonate polymorphs (vaterite and aragonite) resulting from C–S–H carbonation. The pattern then shows a gradual mass loss that ends with a more intense loss around 800 °C, which can be attributed to the decomposition of well-crystallized calcite. The exact temperature for the decarbonation peak(s) depend(s) mainly on the relative amount of calcium carbonate and the fineness of particles. Also, two consecutive overlapping peaks may result from this process, as when larger size grains are heated more time is required for the diffusion of heat and

release of CO₂. Although the mass of CO₂ released per unit mass of calcium carbonate is independent of the grain size and the various forms in which it can be present, it seems that poorly crystallized compounds or grains different in size might be main reasons for underestimation of calcium carbonate content [4]. As long as the signal is attenuated for these reasons, i.e., weight loss is produced more gradually over a more extended temperature range, and the determination of the onset of calcite decomposition is then more difficult to determine precisely. In addition, in the range between 50 and 600 °C, weight loss due to loss of interlayer water and dehydration of C–S–H also takes place simultaneously with the other processes.

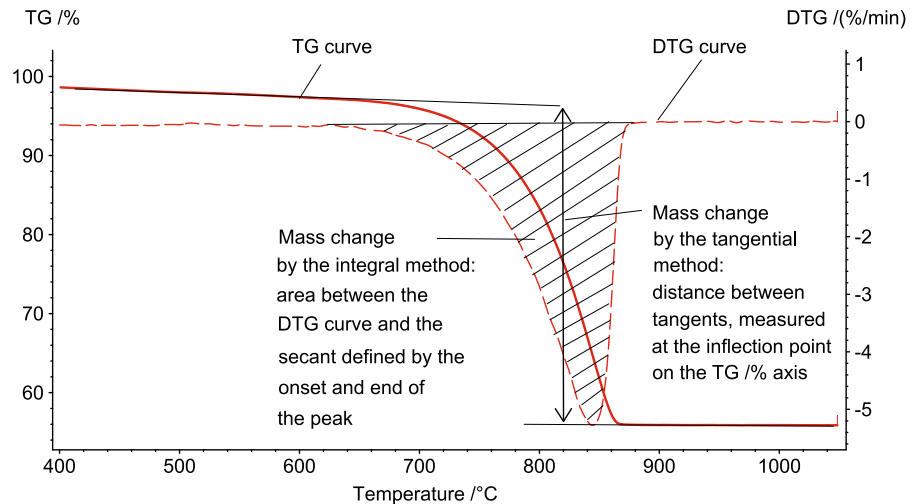


The amount of portlandite is computed from the corresponding weight loss considering that 74.09 g of portlandite releases 18.01 g of water during decomposition. Similarly, the weight loss associated with calcium carbonate decomposition can be used to calculate the amount of calcium carbonate present considering that 100.09 g of CaCO₃ releases 44.01 g of CO₂. The main concern is how these weight losses are determined.

The tangential and integral methods can be applied for this computation (Fig. 1). The tangential method consists in computing the mass loss from the distance, at the inflection point of the signal, between the tangents to the TG curve after and before the change in the slope corresponding to the weight loss step. Alternatively, 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 achieved by integrating the DTG over a determined temperature range or time period, discounting the area over the secant to the curve between the onset and end of the peak, which corresponds to weight loss caused by other processes (in this case, dehydration of C–S–H). For other thermal analysis techniques such as differential thermal analysis (DTA), the interpretation and quantification of the results can be more difficult due to a non-stable base line signal caused by the intrinsic properties of the products obtained during the thermal decomposition of the sample. Then,



Fig. 1 Example of mass loss determined by the tangential and integral methods



decomposition of calcite and portlandite can be better evaluated by DTG than by DTA [8].

Differences in the setup of the measurement (vessel type, heating rate, sample amount, particle size, gas flow rate, purging gas, pretreatments) are frequently reported. This disparity makes the comparison between data in the literature quite difficult as the results of thermal analyses are strongly influenced by the testing features.

A Round-robin test [9] including the quantification of portlandite in pure OPC and quartz, slag and fly ash blended pastes showed a standard deviation of 3 g/100 g of binder for portlandite content among different laboratories. Details of the mixtures can be found in [9]. By comparing the portlandite contents of inert quartz blended pastes with slag/fly ash blended pastes, the reaction degree of slag and fly ash could be computed from the portlandite consumption. The outcomes showed an underestimation of the reaction degree in comparison with other methods such as selective dissolution, BSE image analysis or XRD/Rietveld + PONKCS. One of the possible causes of this underestimation is the underestimation from QTG itself, as the underestimation of portlandite by QTG seems to be consistently proportional to the actual content of it. When these extensive data sets of quantifications of portlandite contents by XRD/Rietveld and by QTG, on blended and unblended cement pastes with curing times between 1 and 90 days, were compared [10], consistent underestimation of QTG with respect to QXRD was obtained (Fig. 2). QTG was able to detect only 87% of the portlandite content

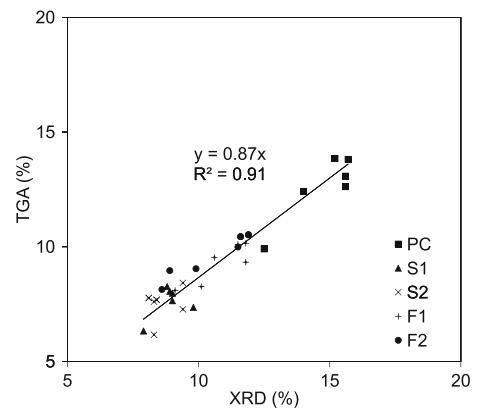


Fig. 2 Portlandite contents in cement pastes from XRD/Rietveld and TG. PC 100% OPC paste, S1 60% OPC + 40% slag paste, S2 60% OPC + 40% slag paste, F1 70% OPC + 30% fly ash paste, F2 70% OPC + 30% fly ash paste. From [10]

determined by XRD/Rietveld. It must be mentioned that XRD analyses were performed including 10% of zincite as an internal standard for computing portlandite contents considering the amount of amorphous or non-identified compounds in the samples (mostly C–S–H and unreacted supplementary cementitious material).

Also De Schepper [11] reported different portlandite contents in slag blended cement pastes when applying different analytical methods. Despite the tangential method seems the most accurate as the concurrent weight loss due to other cement hydrates is considered separately, better correlation for the quantifications based on the total weight loss than on the tangential method was obtained when compared to

values determined by XRD/Rietveld analysis and mass balance from cement hydration. This tendency indicates again a consistent underestimation of portlandite from TG measurements when compared with both XRD/Rietveld analysis and mass balance from alite and belite consumption. In hydrated systems, De Schepper [11] found that the hydration stoppage method has a significant influence on the quantification of portlandite, as it affects mostly the weight loss due to C–S–H dehydration, which overlaps with portlandite dehydroxylation and therefore affects its quantification depending whether this is determined from the total weight loss or by the tangential method. Here, solvent exchange with isopropanol resulted in lower portlandite contents from QTG than freeze drying.

A comparative study of the quantification of portlandite through XRD/Rietveld and TG can also be found in [12]. Mixtures consisted of unhydrated cement intermixed with 15, 20, or 25% of pure portlandite powder. The results of the analyses of these mixtures by XRD and TG showed that both measure amounts very close to the actual composition of the mixture but limited underestimation of the content is achieved for TG more than for XRD. However, this study includes no analysis of the significant effect of the overlapping weight loss from C–S–H, as only unhydrated samples were considered.

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

2 Materials and methods

The experimental part of this study first included the analysis of pure portlandite and calcite by TG, as a procedure for calibration of the device for quantitative analysis. Then, a second stage included the analysis of OPC and OPC + limestone pastes, and siliceous gravel (containing about 15% of carbonate), with and without portlandite and calcite as an internal

standard. The thermogravimetric measurements were performed in a Netzsch STA 449F3 device, heating from room temperature to 1000 °C at a heating rate of 10 °C/min in a dynamic atmosphere of nitrogen at a flow rate of 50 ml/min. Open alumina crucibles were used to contain the sample mass, which was approximately 50 mg each time.

2.1 Standard calibration

Pure portlandite and calcite were used as reference materials. Portlandite was prepared by hydrating analytical quality CaO for 10 min, after which water was removed by filtration. The sample was washed with methanol three times for solvent exchange and finally dried at 80 °C for 15 min. Water was not fully decarbonated, and little carbonation of portlandite occurred during the preparation of this reference material (3.16% of CaCO₃ content, Table 1). Calcite used as an internal standard was a 99.5% analytical reagent grade calcium carbonate.

2.2 QTG with internal standard

Pastes with pure OPC (CEM I 42.5) and OPC + 10% limestone powder were prepared and cured for 28 days at 20 °C and >95% RH. After the curing period, hydration was stopped by drying the pastes at 40 °C for 1 day and subsequent solvent exchange with isopropanol. Afterwards, they were manually ground with mortar and pestle to a maximum size of 63 μm and tested for TG. Measurements for the pure paste/aggregate samples, and samples containing paste/aggregate and 5 or 10% of standard portlandite or calcite were performed. From these measurements, the total portlandite contents with and without internal standard were compared to the added amounts of portlandite. Additionally, samples consisting of a ground gravel aggregate containing carbonates with and without internal standards were analysed.

3 Results

3.1 Standard calibration

Figure 3 presents a comparison of 16 blank correction curves for buoyancy. Here, the correction signal is procured by measuring an empty crucible under



Table 1 Contents of portlandite and calcite determined from weight losses from the tangential method and corrected by factors obtained from pure internal standards (g/100 g sample)

Sample	Portlandite		Calcite	
	Without correction	Corrected	Without correction	Corrected
Standard portlandite	91.47	93.80	3.16	–
Standard calcite	–	–	91.23	–
A(1)	–	–	13.84	15.17
A(2)	–	–	15.11	16.57
A5C(1)	–	–	18.75	20.55
A5C(2)	–	–	17.75	19.46
A10P	7.44	7.93	14.98	16.42
A10C10P	7.52	8.01	21.75	23.84
A10C(1)	–	–	21.93	24.04
A10C(2)	–	–	22.57	24.74
P	13.65	14.54	1.18	1.30
P5C	12.83	13.66	5.75	6.30
P10C	12.09	12.87	9.93	10.89
P5P	16.69	17.78	1.57	1.72
P10P	19.41	20.67	1.68	1.84
L	13.69	14.58	6.73	7.37
L5C	13.16	14.01	11.00	12.06
L10C	13.36	14.23	14.23	15.59
L5P	17.56	18.70	6.20	6.80
L10P	20.19	21.50	6.25	6.85

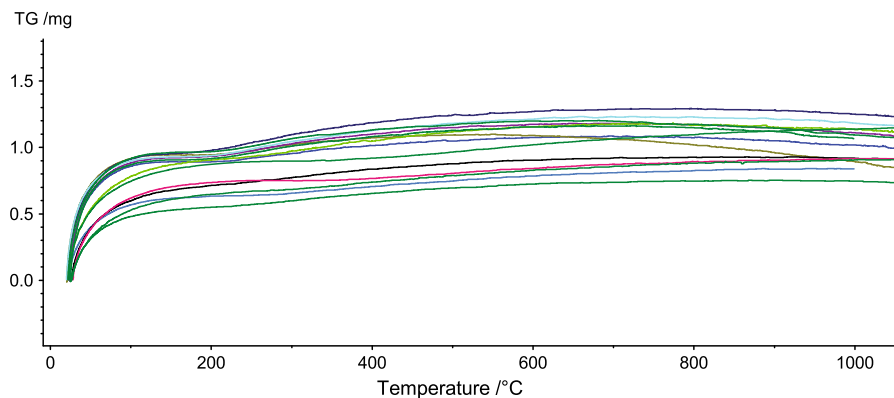


Fig. 3 Blank correction curves ($\times 16$) for buoyancy

exactly the same conditions as used for the analysis of samples. This allows discounting the apparent mass increase due to decreasing gas pressure in the chamber during heating. However the correction for buoyancy improves the reliability of results, some little discrepancies remain always present, and it can be seen that the correction using one or another curve will always end in dissimilar results. It should be kept in mind that the device used in this study employs a vertical

pushrod for the measurements, and the buoyancy implications may be different for devices with other geometries. For the buoyancy correction, 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, but it will certainly never be perfect.

In this respect, TG results for internal standards (portlandite and calcite) corrected for buoyancy are

presented in Fig. 4, where relative total weight losses in the ranges 20–105 °C, 105–1000 °C, and 105–600 °C are presented. Additionally, weight losses by the tangential (Marsh) method [13] and the integral method are computed for the steps corresponding to portlandite dehydroxylation and calcite decomposition. Here, portlandite and calcite weight losses of 0.54 and 2.53% in the ranges 105–350 °C (TG of portlandite) and 105–600 °C (TG of calcite), respectively, are observed. These losses are unrelated to decomposition of portlandite or calcite, and cannot be linked with the composition of these compounds. Instead, it seems that this reduction is an artifact caused by the correction for buoyancy, which is not exactly the same for the blank and the measurement of the samples. This artifact would be relatively higher for smaller amounts of sample being tested, as it comprises a net value that is then referred to the sample weight. 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. This conflict means that no individual distinction is possible in that case. Then, despite a weight loss virtually induced by the correction with 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.

3.2 QTGA with internal standard

Figures 5, 6 and 7 present results with/without internal standard from OPC and OPC + limestone pastes, and ground gravel aggregate, respectively. For pastes, peaks for DTG around 120, 170, 450 and 750 °C are noted in association with the 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 internal standard 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 grain sizes of the calcite from limestone and the calcite added. It is also possible that this differentiation is due to the presence of minor constituents containing Mg in limestone. 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.

The addition of similar amounts of portlandite and calcite causes a more significant change in the signal for calcite than for portlandite, in correspondence with the corresponding weight loss associated to each compound (24.3% for portlandite vs. 44% for calcite). However, it can also be noted that whereas the addition of portlandite causes no significant change for

Fig. 4 TG measurements for portlandite (green) and calcite (red); signals corrected for buoyancy

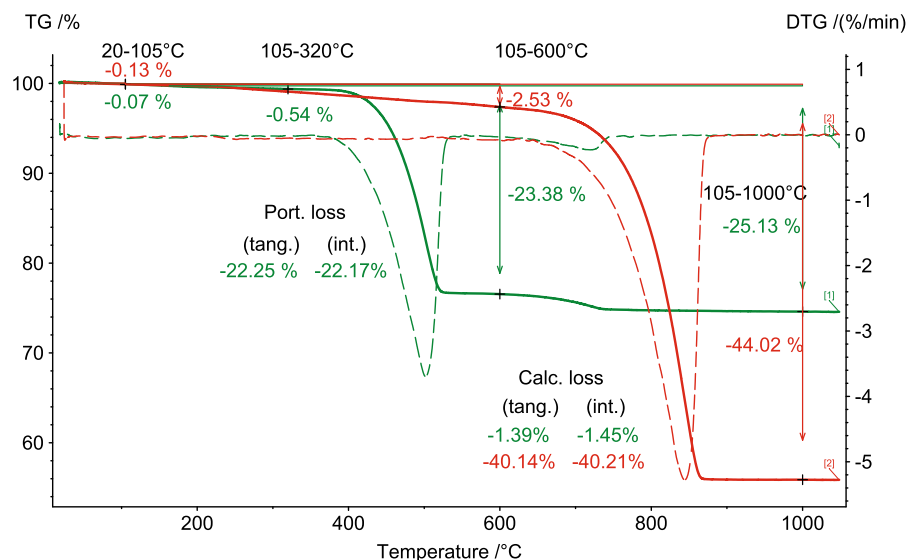


Fig. 5 TG for limestone blended paste with and without internal standard. *L* Pure paste, *L10P* 90%paste + 10% portlandite, *L10C* 90%paste + 10% calcite, *L5P* 95%paste + 5% portlandite, *L5C* 95%paste + 5% calcite

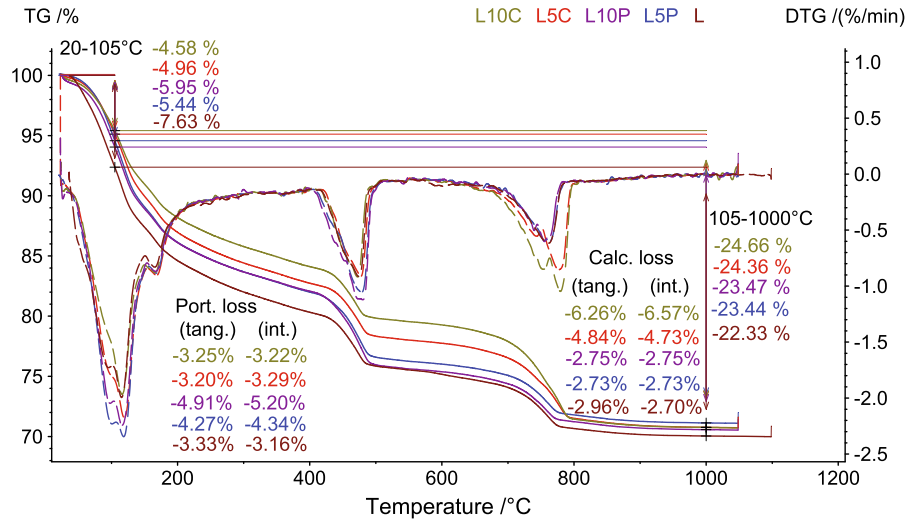
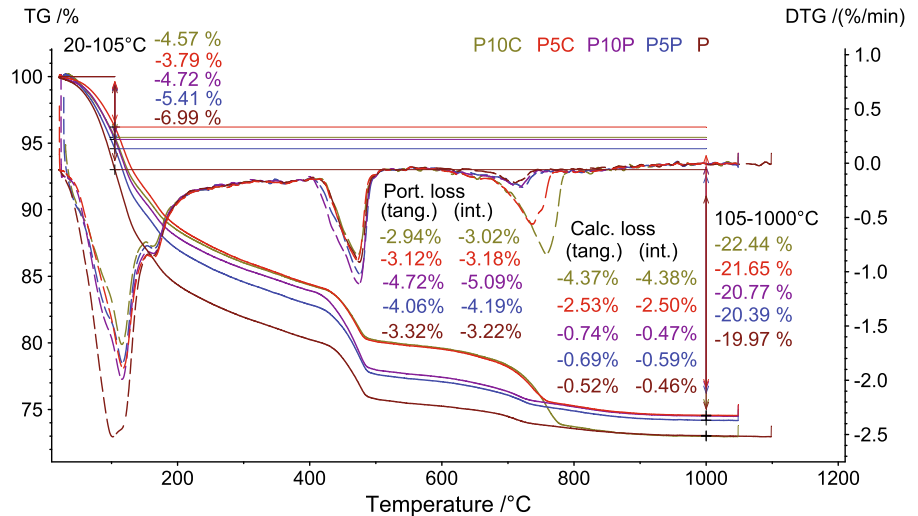


Fig. 6 TG for OPC paste with and without internal standard. *P* Pure paste, *P10P* 90%paste + 10% portlandite, *P10C* 90%paste + 10% calcite, *P5P* 95%paste + 5% portlandite, *P5C* 95%paste + 5% calcite



the position of the peak in the DTG, calcite causes a shift towards higher temperatures in accordance with the amount added.

4 Discussion

From the weight losses computed by the tangential method for portlandite and calcite, the corresponding quantified amounts of these phases are presented in Table 1. For samples consisting of internal standard, and aggregate with/without added internal standard, only one decomposition reaction at a time takes place during heating (i.e., there is no C–S–H in the samples). For these samples, the tangential method should

theoretically lead to the same amount as obtained from the total weight loss (i.e. the start and the end parts of the signal should be horizontal in the graph), but this is not the case. As expected, the total weight losses from TG for standards (44 for calcite and 25.1% for portlandite) are remarkably consistent with full decomposition of pure compounds, corresponding to quantifications of 100 and 100.7% of calcite and portlandite, respectively. Here, the reported amount of portlandite includes the equivalent amount to the 3.16% of carbonated material determined by TG. On the other hand, when the tangential method is applied the amounts of calcite and portlandite are underestimated by factors of 0.912 and 0.915 (+0.023 of carbonated material), respectively. It is important to mention that



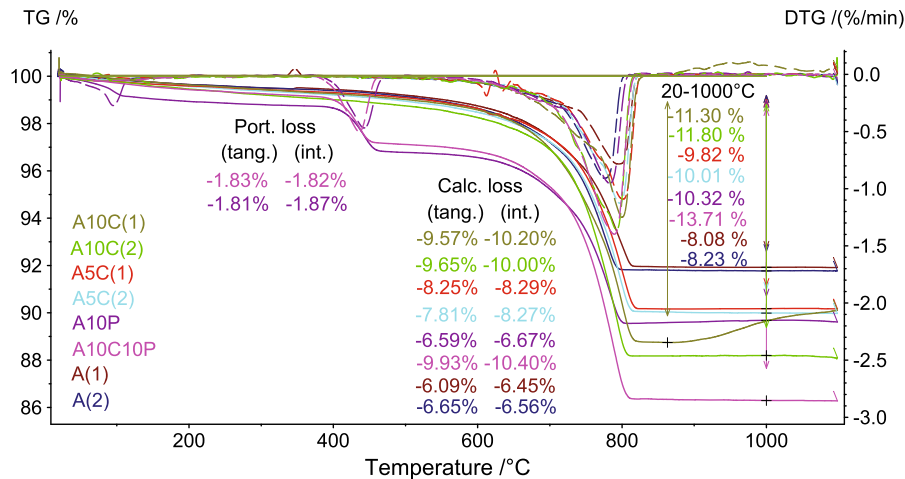


Fig. 7 TG for aggregate with and without internal standards. *A(1)* pure aggregate, *A(2)* pure aggregate, *A5C(1)* 95%aggregate + 5% calcite, *A5C(2)* 95%aggregate + 5% calcite, *A10P*

90%aggregate + 10% portlandite, *A10P10C* 90%aggregate + 10% portlandite + 10%calcite, *A10C(1)* 90%aggregate + 10% calcite, *A10C(2)* 90%aggregate + 10% calcite

despite the computation is implemented in the instrument software, there is still some influence of the operator input on the definition of the onset and end of the temperature range (e.g., the elimination of signal noise, the selection of the temperature range in which the measurement curve points must be identified).

The previous values were used as correcting factors applied to the determinations on pastes with internal standards (Table 1). Still, the differences between the measurements with internal standard and those without internal standard are a little dissimilar than the added amounts of portlandite and calcite. The correction factor for the underestimation obtained from the standard sample is proved to increase accuracy, whereas some differences remain due to the precision of the method.

Alternatively, the quantification based on the integration over the DTG curve is considered, and the results are presented in Table 2. It should be remembered that this computation only considers the area of the corresponding peak (i.e., the computed area is the one between the DTG curve and the secant between the onset and end of the peak). Although from a mathematical point of view this is the same procedure to that of the tangential method, the method based on the integration over the DTG curve is more precise for low contents. The main reason is that the onset and end of the peaks in DTG curves are easier to be determined than the change in the slope of the TG required for the tangential method, as exemplified in

Fig. 8. Moreover, the integral method offers a better traceable quantification than the tangential method and is less affected by the noise in the signal.

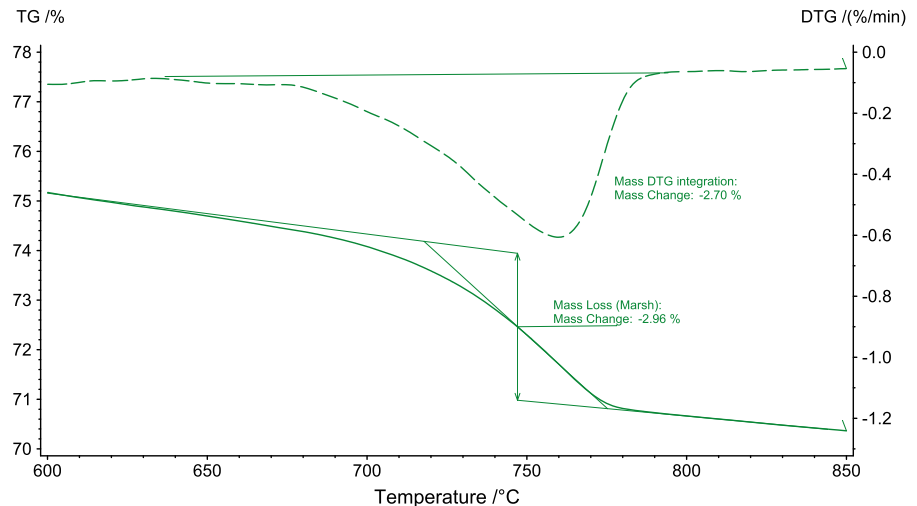
Finally, Table 3 shows the average relative amounts obtained from the results for each of the studied internal standards obtained for each quantification method. For some samples, lower quantification ratios for portlandite in comparison with calcite were obtained, and this would be mostly due to the instability of portlandite when in contact with the atmosphere during blending and setting of the measurement, when some carbonation might have occurred despite the precautions taken. It can be seen that between 84.5% (for 10% portlandite added and measured by the tangential method) and 103.8% (for 5% portlandite added and measured by the integral method) of the added internal standards were quantified. These ratios could be used as secondary calibration factors for future measurements, which are already including the primary calibration factors derived from the analyses of pure compounds. However, this seems unnecessary if it is considered that the variation of results is indicating the level of precision of the methodology for quantifying portlandite and calcite in cementitious materials.

Thus, the use of 5% of calcite as internal standard seems the most convenient procedure. Calcite is more stable than portlandite when exposed to the atmosphere, and there is no significant difference in the ability of TG for quantifying a similar relative content

Table 2 Contents of portlandite and calcite determined from weight losses from the integration method and corrected by factors obtained from pure internal standards (g/100 g sample)

Sample	Portlandite		Calcite	
	Without correction	Corrected	Without correction	Corrected
Standard portlandite	91.16	93.59	3.30	–
Standard calcite	–	–	91.39	–
A(1)	–	–	14.66	16.04
A(2)	–	–	14.91	16.31
A5C(1)	–	–	18.84	20.62
A5C(2)	–	–	18.80	20.57
A10P	7.69	8.43	15.16	16.59
A10C10P	7.48	8.21	23.52	25.74
A10C(1)	–	–	23.23	25.42
A10C(2)	–	–	22.75	24.89
P	13.24	14.52	1.05	1.14
P5C	13.08	14.34	5.68	6.22
P10C	12.42	13.62	9.95	10.89
P5P	16.82	18.45	1.34	1.47
P10P	20.93	22.96	1.07	1.17
L	12.99	14.25	6.14	6.71
L5C	13.53	14.84	10.75	11.76
L10C	13.24	14.52	14.93	16.34
L5P	17.48	19.17	6.20	6.79
L10P	21.38	23.46	6.25	6.84

Fig. 8 Comparison between quantification from tangential method on TG and integral method over DTG. P1285P sample



of one or the other. This calibration procedure was able to compensate underestimation from TG, and it is a positive approach for increasing reliability of results. Besides, the precision of the method including this calibration procedure can be expected in the range of ± 10 and $\pm 5\%$ in relation to the actual content for portlandite and calcite, respectively.

5 Conclusions

The calibration method proposed allowed an increased reliability of the quantification of both portlandite and calcite in hydrated cement pastes. The accuracy was also improved when the quantification of portlandite and calcite was based on the weight loss determined by

Table 3 Means and standard deviations for relative amounts of internal standard obtained for the tangential method on the TG curve and the integration method on the DTG curve (g/100 g sample)

Sample	Portlandite		Calcite	
	5.00	10.00	5.00	10.00
Amount added	5.00	10.00	5.00	10.00
Amount computed (%)				
Tangential method	5.08 ± 0.26	8.45 ± 0.34	5.03 ± 0.33	9.55 ± 0.33
Integration method	5.18 ± 0.26	9.31 ± 1.14	5.19 ± 0.15	10.26 ± 0.52

the integration of the DTG instead of using the tangential method.

With the calibration based on the analysis of pure compounds, the quantified amounts for calcite and portlandite tend to slightly underestimate the actual contents in the samples, with higher differences for portlandite than for calcite. A calibration of the device with pure portlandite and calcite is recommended, but a precision of ± 10 and $\pm 5\%$ of the actual content of portlandite and calcite, respectively, should be expected for this application of quantitative thermogravimetry. The correction factors obtained with previous analyses of cement pastes with an internal standard can be applied to the weight loss computed by the tangential or the integral methods.

The integral method over the DTG curve is more precise than the tangential method applied on the TG, as the decomposition of compounds is more easily identified by the operator as a difference in the vertical magnitude in DTG rather than a difference in the angle of the slope in TG. Therefore, traceable and more precise results can be expected, especially for calcite content where the onset temperature is especially difficult to identify due to the very gradual release of CO_2 .

Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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